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# FUNDAMENTAL IGNITION STUDY FOR MATERIAL FIRE SAFETY IMPROVEMENT

K.L. PACIOREK AND L.B. ZUNG

FINAL REPORT, PART I  
CONTRACT NASW-1921

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION  
MATERIALS ENGINEERING BRANCH  
WASHINGTON, D. C. 20546

AUGUST 31, 1970

**DYNAMIC SCIENCE**



A Division of Marshall Industries

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## FOREWORD

This Summary Report describes the work performed at Dynamic Science, a Division of Marshall Industries, under NASA Contract NASW-1921 during the period July 7, 1969 to July 7, 1970. The investigations were performed by K. L. Paciorek, L. B. Zung, and Jacquelyn Kaufman. The work was administered under the direction of Ames Research Laboratories, with Dr. Domenick Cagliostro furnishing technical guidance.

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## SUMMARY AND RECOMMENDATIONS

The present study embodied the investigation of preignition, ignition, and combustion characteristics of Delrin (acetate terminated polyformaldehyde) and Teflon (polytetrafluoroethylene) resins in air and oxygen. This work involved the determination of ignition limits and their dependence on temperature and the oxidizing media as well as the analyses of the volatiles produced. To attain a better understanding of the operative processes and mechanisms a limited number of tests were conducted in argon, an inert medium, where only purely pyrolytic reactions can take place. All these experiments were performed using the stagnation burner arrangement which was designed and constructed under this contract. This system afforded a laminar gas flow of well defined temperature profile and allowed an independent variation of polymer heating block and gas temperatures. The construction permitted ready insertion of a sampling probe and was sufficiently flexible to be adaptable to investigation of various materials. To extend the data thus accumulated to a variety of different materials, a theoretical treatment of the ignition and combustion phenomena was devised. Its applicability to real situations can be tested once sufficient information becomes available to define the operative limits.

Based on the current investigation it was found that in the case of Delrin the ignition and ignition delays are apparently independent of the gas (air, oxygen) temperatures. The ignition limit was found to lie in the vicinity of 386°C for the oxygen and ca 500°C for the the air system. The ignition governing step was found to be the dissociation of formaldehyde into carbon monoxide and hydrogen. The results generated indicate that hydrogen is the ignition triggering agent. It should be pointed out that a certain degree of oxidation does occur prior to ignition.

The Teflon studies are not complete because of time limitation. Consequently, ignition limits were established in oxygen only. The ignition in oxygen would seem to be somewhat gas temperature dependent, although the block temperature is definitely the governing factor. The limits found were: oxygen 564°C, block 501°C; oxygen 471°C, block 525°C. In pure oxygen even prior to ignition no Teflon monomer was detected, whereas the

quantities of  $\text{COF}_2$  produced were relatively small. In air, where ignition occurred only considerably above  $550^\circ\text{C}$ , significant amounts of  $\text{COF}_2$  were found, even in the absence of ignition, (ca 50% of the depleted Teflon was in the form of  $\text{COF}_2$ ). The rate of formation corresponded to 0.15% Teflon/sec consumed in the production of  $\text{COF}_2$ .

The investigations of ignition characteristics of Teflon in air are to be continued, together with the analyses of the products formed on ignition and during combustion. As described above, toxic off-gassing was found to occur in Teflon without concurrent ignition or burning. Thus it would appear necessary in future examinations of other materials to pay particular attention to preignition reactions and their dependence on oxygen concentration and temperature. In a similar manner appraisal of additives and their effect on the mechanism of decomposition in oxidizing media has to be undertaken. The limited study conducted to date has definitely shown that better understanding of the underlying processes can yield information of great importance in practical situations, where fire and toxicity hazards cannot be tolerated.



## INTRODUCTION

There are a number of factors which need to be considered when investigating the flammability and toxicity aspects of materials. A truly meaningful study requires, among others, the designing and construction of equipment to allow the performance of actual tests under rigidly controlled conditions. The selected experiments have to be conducted with provisions for sampling prior to ignition, at ignition, and during actual combustion.

One of the objectives of such an investigation is to determine for the chosen materials ignition limits in oxidizing media of interest and their dependence on temperature profiles. The gas analyses at the various stages of pyrolysis, ignition, and combustion in different atmospheres, based on the type and concentration of the species present should allow the operative mechanisms to be elucidated. The nature of the products formed and their rate of production should be also indicative of the toxic effects, if any, and their importance in material consideration for a particular application.

To extend a specific, limited study to a variety of problems to be encountered in the use of various materials under widely differing conditions, there is a definite need to devise theoretical postulations based on flow, temperature, and material variables. Once a sufficient number of actual experimental data are accumulated the practical applicability of such a theoretical system can then be tested.

The accumulation of ignition, decomposition, and pyrolysis characteristics of a sufficiently large number of related substances should permit the tailoring of material properties for a specific application.

Under the present program using a stagnation burner arrangement, studies were performed on Delrin and Teflon resins in oxygen, air, and argon atmospheres. Based on these investigations, which are described in the Technical Discussion Section of this report, ignition limits were determined and mechanisms operating during pyrolysis, ignition, and combustion were postulated. From the nature of the products evolved, the probable toxic effects were deduced. An attempt was made to delineate a broad theoretical treatment adaptable to a variety of problems associated with flammability considerations.

## TECHNICAL DISCUSSION

For the clarity of presentation this section has been divided into three main parts:

Experimental Details and Procedures: description of apparatus and techniques used in burning the polymers, together with the discussion of analytical procedures employed.

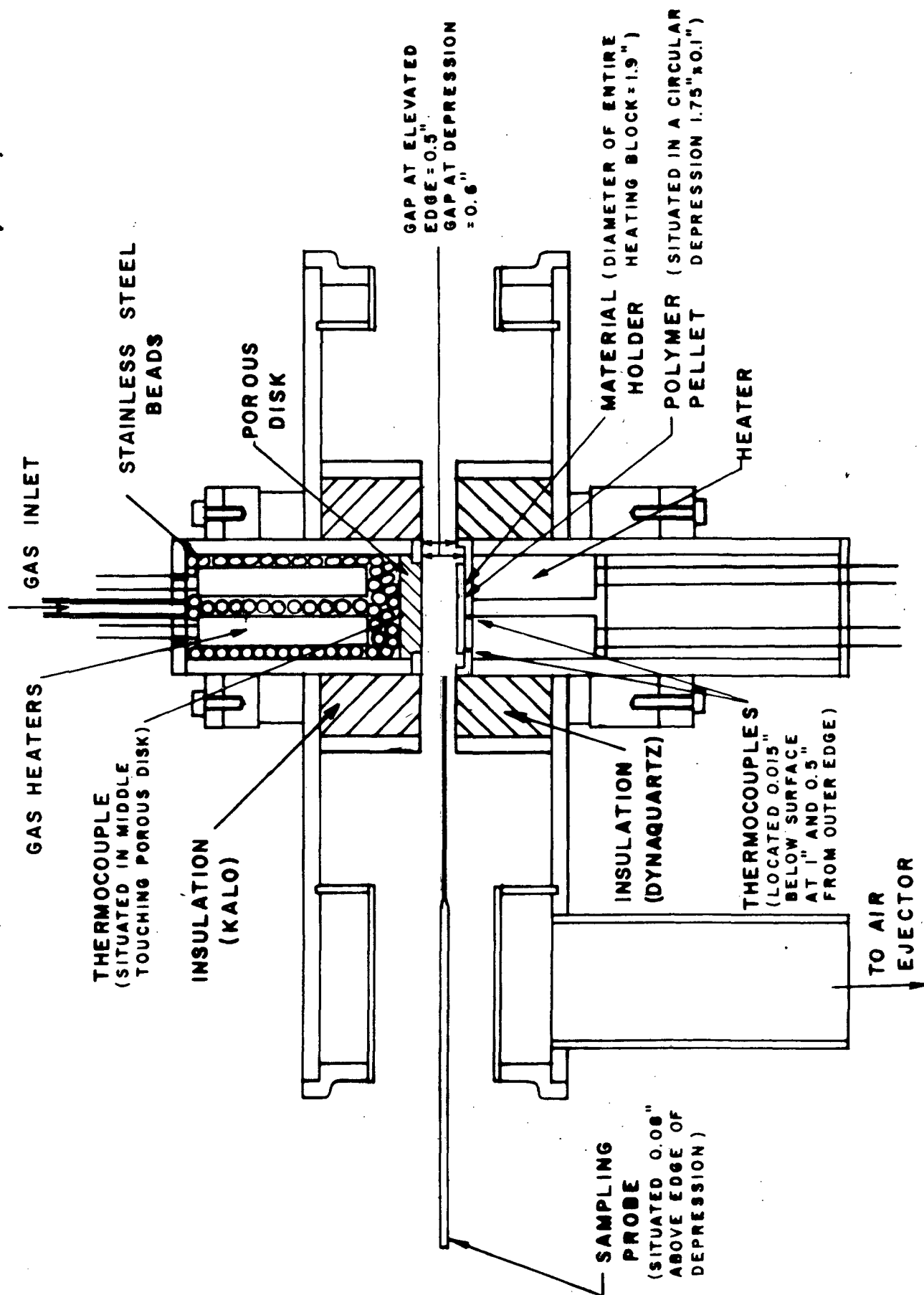
Polymer Study: results and discussion of the investigations performed on Delrin and Teflon polymers using the stagnation burner approach.

Theoretical Considerations: a purely mathematical treatment of the occurring processes from the fluid mechanics point of view.

### Experimental Details and Procedures

Apparatus and its Operation. - The preignition, ignition combustion, and pyrolysis studies were performed using a Stagnation Burner where oxidizing gas is introduced to flow over the polymer pellet in a direction perpendicular to the polymer surface. In Figure 1 the Schematic of the final version of the Stagnation Burner is given together with the quartz sampling probe in place. This arrangement ensured laminar gas flow. In view of the open structure of the system all the tests were performed at atmospheric pressure. The gaseous atmospheres investigated were air, oxygen, and argon. The gas inlet pressure was kept constant at 90 psi in all the tests. The gas flow rate is measured by a turbine type flow meter. However, in view of the gas temperature range 200 - 700°C, the actual gas flow varied from 145.6 - 299.4 cc/sec (8.88 - 18.27 inch<sup>3</sup>/sec).

The gas sampling probe is depicted in Figure 2. During the run, all the three ampoules were in place. Prior to the insertion of the polymer pellet the probe itself was placed in the burner, as shown in Figure 1, and it was pumped via the 4 mm stopcock. Each of the ampoules was previously evacuated on the vacuum line. During sampling the 4 mm stopcock to the vacuum pump was closed and each ampoule was opened to the probe for 5 seconds. Between sampling the system was evacuated via the 4 mm stopcock. This time interval varied usually between 3 and 5 seconds although in some special experiments much longer time intervals were employed. All these details will be fully discussed in section "Polymer Study."



## STAGNATION BURNER

Figure 1. Stagnation Burner with Polymer Pellet and Sampling Probe in Place.

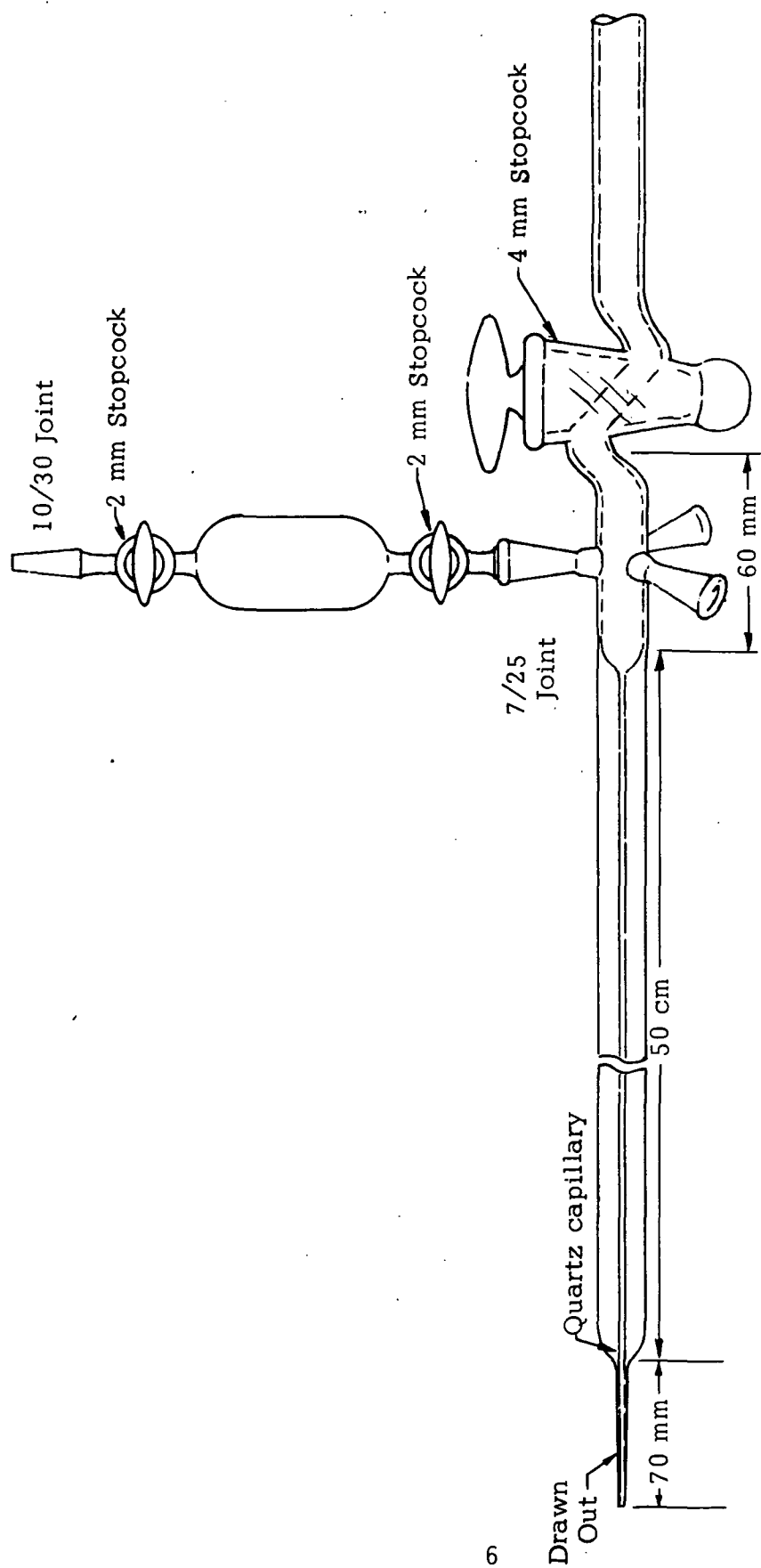


Figure 2. Sampling System

All the tests involving the Stagnation Burner were performed after steady state was reached, i.e., after the gas and the heating block have attained constant temperature. The temperatures of gas and the heating block were varied independently and were measured by the thermocouples positioned as shown in Figure 1. These were calibrated using melting points of pure materials in the temperature range of interest. All the temperatures given in the Tables in section "Polymer Study," are the temperatures recorded on CEC model 5-124A recording oscillograph just prior to sample injection. However, during a number of selected runs including every run where sampling was done, a complete temperature profile (of gas and heating block) was obtained using the CEC oscillograph.

The majority of Delrin tests were performed with the fume hood, where the apparatus is situated, in the off position. However, in the Teflon series, in view of the toxic nature of the products, initial tests were conducted with the fume hood on, leading to a certain degree of temperature fluctuation and mixing of the reaction gas with the ambient atmosphere.

The onset of ignition was determined by visual means, namely when flame was first observed. The rise of temperature, as seen from the heating block temperature trace of the oscillograph, was a secondary means of ignition onset recognition. However, this latter technique exhibited a delay of several seconds (2-4) as compared to the visual observation.

Temperature Profile. - In Figure 3 the temperature profile of the flow field is given. This was obtained by allowing high temperature air streams to flow over the material holder which was kept at room temperature. A 0.005" movable thermocouple was used to map the temperature profile. In the prototype system, where the measurements given in Figure 3 were taken, there was a significant gas temperature drop ( $460^{\circ}\text{C}$  at center to  $410^{\circ}\text{C}$  at the edge) since originally the gas inlet channel was not insulated. However, since the sample is approximately centered in the holder the gas temperature variation above the sample, as shown in Figure 3, was of the order of  $10^{\circ}\text{C}$ . In the present system, where all the reported tests were performed, the actual temperature gradient must be significantly lower than the  $10^{\circ}\text{C}$  in view of the additional insulation.

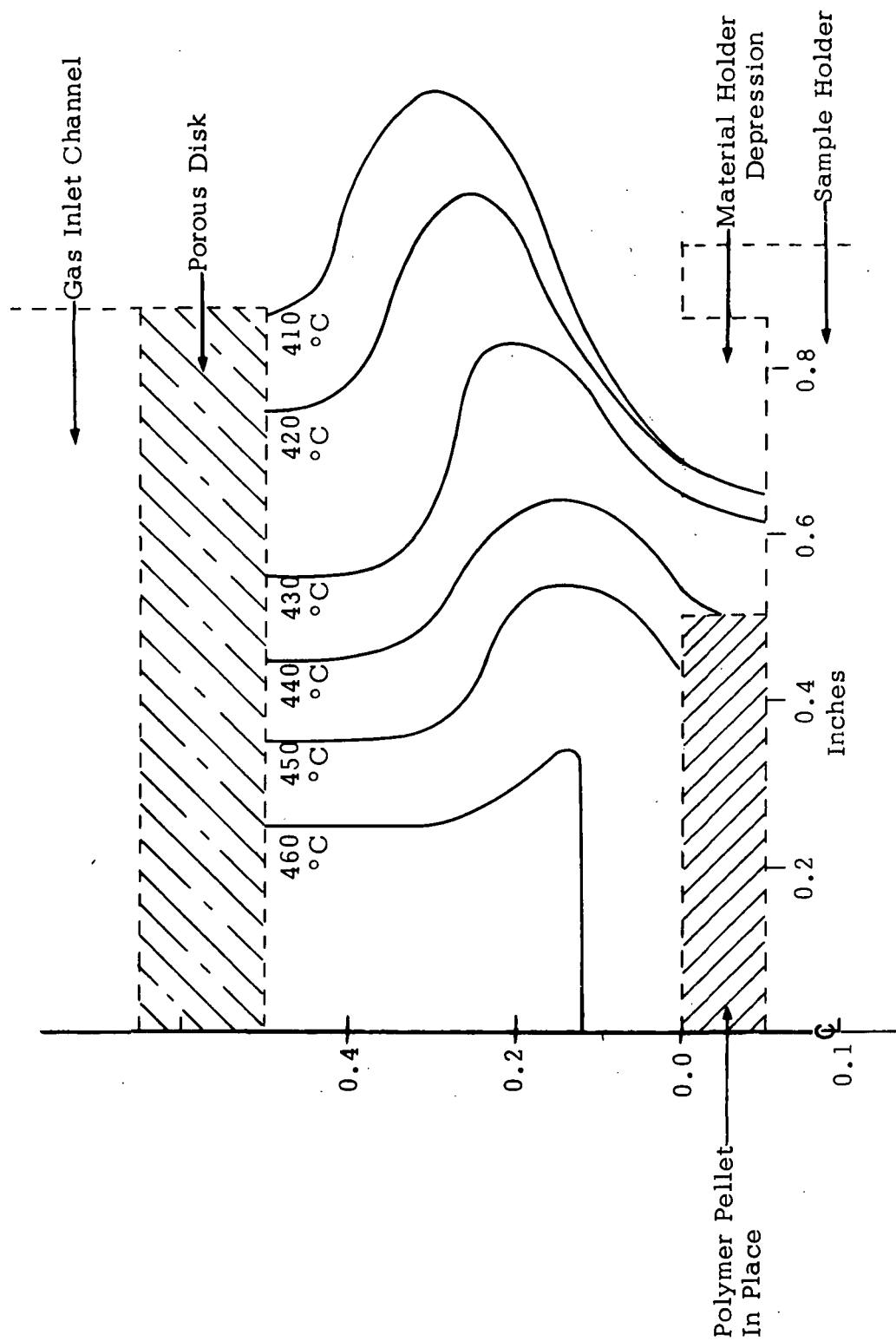


Figure 3. Isotherms of the Stagnation Flow Field.

Polymeric Materials. - Two materials were investigated with respect to their preignition, ignition, and combustion characteristics, namely Delrin and Teflon resins.

The Delrin acetal resin employed was the DuPont Delrin resin 500, purchased in the rod form of 1.00" diameter and machined into 1.00" O.D. x 0.100" thick pellets. Average weight =  $1.867 \pm 0.019$  g.

The Teflon (polytetrafluoroethylene) resin employed was the DuPont grade 7 TFE resin. Four types of pellets were obtained:

1/2" diameter 0.01" thick	average weight $65.7 \pm 0.3$ mg
1" diameter 0.01" thick	average weight $257.9 \pm 0.1$ mg
1/2" diameter 0.05" thick	average weight $346.5 \pm 4.0$ mg
1" diameter 0.05" thick	average weight $1391.1 \pm 12.6$ mg.

The 0.01" thick wafers were cut out from a sheet, whereas the 0.05" thick pellets were machined from 1/2" and 1" diameter rods. The 0.01" wafers were initially tested, since it was feared that the reaction with oxygen might be of a violent nature. In actual experimentation it was found that the ignition and combustion occurred in a very controlled manner; accordingly the majority of the studies to determine the onset of ignition were conducted with the 1/2" x 0.05" pellets, whereas in the sampling runs the 1" x 0.05" pellets were employed.

Analytical Procedures. - The gaseous atmosphere above the heated polymer block was sampled using the quartz probe, as shown in Figure 2. The gas was collected in the previously evacuated ampoules, using the procedure described in paragraph on "Apparatus and its Operation," subsequently the ampoules were removed from the probe arrangement for specific analyses. Originally gas chromatography separations were attempted. In the case of Delrin for the determination of  $\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{CH}_4$ , and  $\text{CO}$ , a two column system was assembled. Column A, "internal" 4'x1/4" packed with silica gel at 115°C and Column B, "external" 6'x1/4" packed with molecular sieves 13X, at room temperature; whereas, for the determination of  $\text{CH}_2\text{O}$ ,  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$ , and  $\text{HCOOH}$  a 4'x 1/4" Porapak T column at 118°C was employed. Difficulties were encountered in preparing gaseous formaldehyde (Refs. 1, 2) for calibration and actual sample analyses showed the futility of all these arrangements inasmuch as only traces of gaseous  $\text{H}_2\text{CO}$  were collected in the oxygen runs; furthermore, formic acid

was produced also in trace quantities only. No  $\text{CH}_3\text{OH}$  appeared to be formed. Subsequently all the gas analyses were conducted using mass spectrometry (CEC mass spectrometer model 21-620). Each component was calibrated individually for sensitivity at base peak and for breakdown pattern. This applies to the degradation and oxidation products both of Delrin and Teflon. The only compound reported which was not directly calibrated is  $\text{COF}_2$ ; its breakdown pattern and sensitivity were obtained as an average of several mass spectra where it was present as a significant component. All the components given in Tables of mass spectral analyses are presented in mole per cent. In the case of Delrin the amount of solid formaldehyde, deposited on the ampoule wall, was obtained by weight difference between the evacuated ampoule before and after sampling.

#### Polymer Study

Delrin Investigations. - Delrin (an acetate terminated polyformaldehyde) is one of the relatively few polymers which at moderate temperatures unzip into the monomer (Ref. 3).



However, the analytical determination of the formaldehyde monomer is very difficult in view of its ready polymerization (Refs. 1, 2, 5, 6). This polymerization is promoted by oxygen at ca  $300^\circ\text{C}$  as was shown by Spence and White (Ref. 2). Formic acid (Ref. 5) and water (Ref. 1) appear to exert a similar action. These catalytic ingredients namely oxygen and water are present during the heat treatment of Delrin in oxidizing atmospheres such as air and/or oxygen.

The studies performed during this program were aimed at determining the ignition limits of Delrin in oxygen and air and elucidating the mechanism of ignition, or rather the chemical processes occurring prior to and at ignition.

**Experimental Results and Discussion:** All the studies performed on Delrin used the one inch pellet and the reaction procedures followed the descriptions given in the section "Experimental Details and Procedures."



To obtain the ignition limits for Delrin in oxygen a number of tests were performed and these are compiled in Table I. A graphical representation of these results is given in Figure 4. Based on these rather limited data it can be postulated that the ignition is relatively independent of the gas, in this case oxygen, temperature. The polymer heating block temperature would seem to be the ignition determining factor. Thus the ignition limit, in oxygen, (in the system employed) was found to be ca 386°C (heating block temperature). Examining the Table I in particular runs 379-381, 384, 386, and 387, it is clear that at these limiting temperatures the ignition becomes ill defined and the burning period is of a very short duration. Actually, the ignition occurs when most of the fuel, one can visualize the evolved formaldehyde as a fuel, is almost gone. Test 531 would seem to be an exception since here at the low oxygen and heating block temperatures (294 and 387°C respectively) a relatively early ignition with normal burning time took place. On the other hand, we did notice that some of the ignitions seemed to be triggered by what would appear to be a tiny particle (metallic) impurity possibly introduced during pellet machining from the rod. Above ca 420°C (polymer heating block temperature) the ignition took place in a predictable manner. The ignition delay can be roughly correlated with the heating block temperature, as can be seen from Figure 5, although this reproducibility is by no means perfect. Varying the oxygen temperature and keeping the block temperature constant, runs 407, 408, 412, and 452 failed to affect the ignition delay. This would imply that within certain limits the ignition delay is independent of the gas temperature. Unfortunately, these limits are not well defined due to insufficient data.

The ignition limits in air were found to be higher than in oxygen, which is to be expected. Again, the ignition appeared to be dependent primarily on the polymer heating block temperatures, the lower limit being: heating block 500°C, gas 660°C, and the higher limit: heating block 508°C, gas 408°C. The tests performed in air are summarized in Table II, whereas the graphical representation of the ignition dependence upon heating block and gas temperature is given in Figure 6.

**TABLE I. - SUMMARY OF EXPERIMENTS CONDUCTED  
ON DELRIN IN OXYGEN ATMOSPHERE<sup>a</sup>**

Run No.	Gas Temp. °C	Block Temp. °C	Ignition Onset Sec(b)	Burn Time Sec (c)	Remarks
365	543	513	14	41	- - -
367	543	480	41	34	- - -
368	542	476	45	32	- - -
369	542	478	51	34	- - -
370	546	483	23	41	- - -
371	544	478	37	25	- - -
372	544	473	40	40	- - -
373	546	469	45	35	- - -
374	543	446	37	38	- - -
375	515	439	55	37	- - -
377	506	435	50	37	- - -
378	496	428	50	37	Sampling run, sample No.3 taken 10 sec prior to ignition
379	562	388	95	5	At 40 sec, dense, white smoke
380	590	388	115	5	At 35 sec, dense, white smoke
381	595	386	145	1	At 45 sec, dense, white smoke
382	425	389	n.i. <sup>d</sup>	n.a. <sup>e</sup>	At 65 sec, dense, white smoke
384	424	402	170	1	At 65 sec, dense, white smoke
385	426	404	105	45	At 70 sec, dense, white smoke
386	426	412	135	5	At 65 sec, dense, white smoke
387	426	414	155	4	At 65 sec, dense, white smoke
389	440	422	70	40	At 55 sec, smoke visible
390	445	424	57	42	At 50 sec, white smoke

TABLE I.- (Continued)

Run No.	Gas Temp. °C	Block Temp. °C	Ignition Onset Sec (b)	Burn Time Sec (c)	Remarks
392	442	420	90	5	At 55 sec, white smoke
393	434	440	37	43	---
395	440	444	36	40	---
396	440	441	36	42	---
397	441	440	45	39	---
398	437	437	33	44	Sampling run; sample No. 3 at ignition
399	345	427	100	25	At 55 sec, evolution of smoke
400	347	428	61	38	Dense smoke at 60 sec
401	350	429	43	42	---
403	350	427	35	44	---
404	354	429	42	42	---
407	347	450	33	40	---
408	348	450	34	45	---
410	345	456	34	39	---
411	357	459	15	50	Sampling run; sample No. 1 at ignition
412	184	450	35	43	---
413	192	452	34	43	---
414	194	453	22	46	---
415	196	453	23	50	---
416	201	453	23	41	Sampling run; sample No. 3 at ignition
513	238	269	n.i.	n.a.	Complete evaporation in 12 min
515	324	305	n.i.	n.a.	Complete evaporation in 6 min
516	317	316	n.i.	n.a.	Complete evaporation in 5 min 40 sec
517	331	314	n.i.	n.a.	Complete evaporation in 5 min 30 sec
520	389	315	n.i.	n.a.	Complete evaporation in 4 min 15 sec

TABLE I.- (Continued)

Run No.	Gas Temp. °C	Block Temp. °C	Ignition Onset Sec (b)	Burn Time Sec (c)	Remarks
521	439	307	n.i.	n.a.	Complete evaporation in 3 min 30 sec
522	446	310	n.i.	n.a.	Complete evaporation in 3 min 15 sec
523	469	336	141	4	- - -
524	473	337	170	5	- - -
525	434	327	155	5	- - -
526	427	325	n.i.	n.a.	Complete evaporation in 3 min
527	380	313	n.i.	n.a.	Complete evaporation in 3 min 30 sec
529	275	336	n.i.	n.a.	Complete evaporation in 3 min 50 sec
530	280	359	n.i.	n.a.	Complete evaporation in 3 min 40 sec
531	294	387	73	40	- - -
532	312	371	n.i.	n.a.	Complete evaporation in 3 min
533	333	382	n.i.	n.a.	Complete evaporation in 2 min 30 sec
534	343	386	n.i.	n.a.	Complete evaporation in 2 min 35 sec

<sup>a</sup>All the temperatures were recorded just prior to Delrin insertion.

<sup>b</sup>Time measured from insertion of Delrin pellet.

<sup>c</sup>Time from ignition onset to conclusion of burning.

<sup>d</sup>No ignition.

<sup>e</sup>Not applicable.

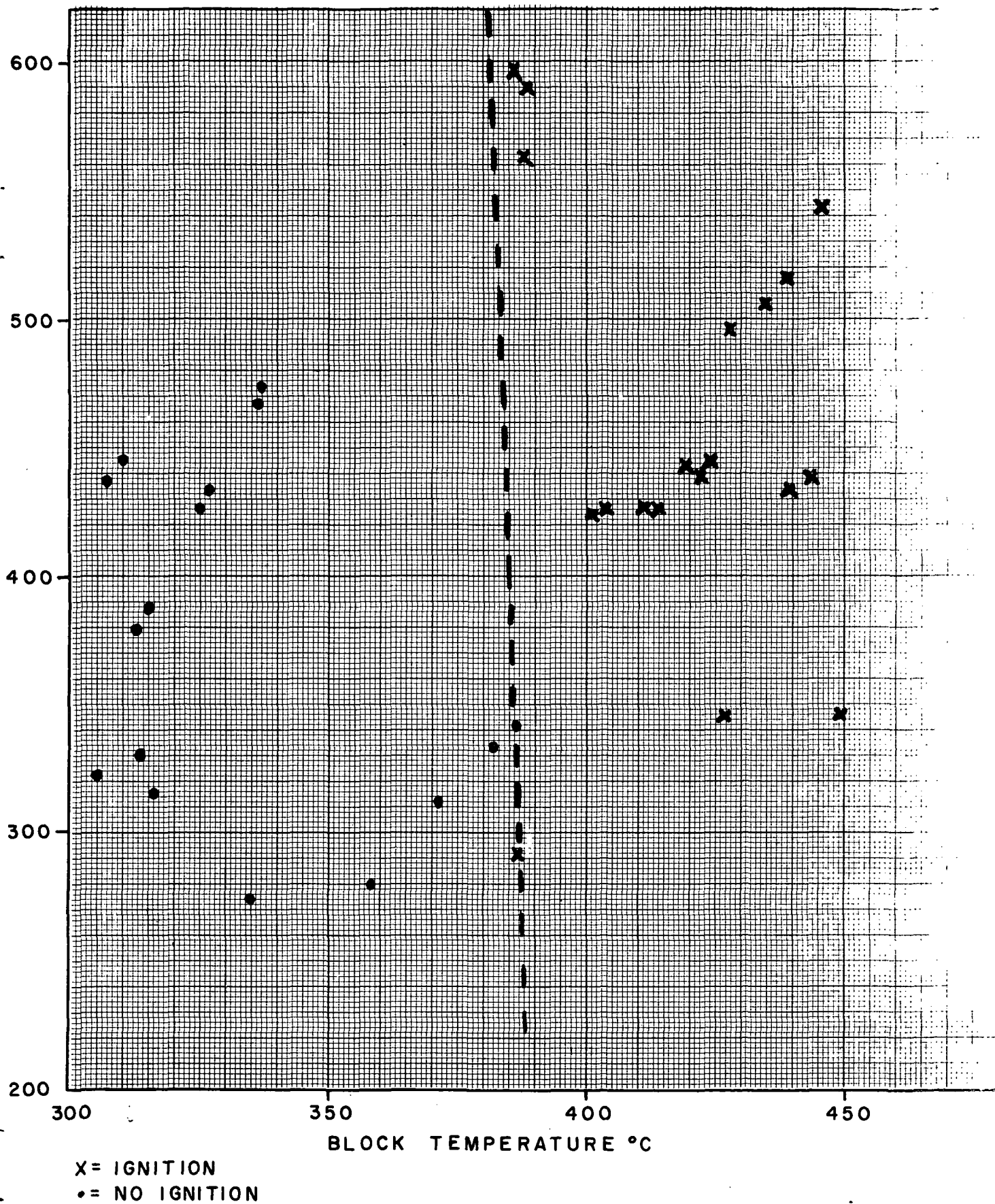


Figure 4. Effect of Polymer Heating Block and Oxygen Temperature Upon Delrin Ignition.

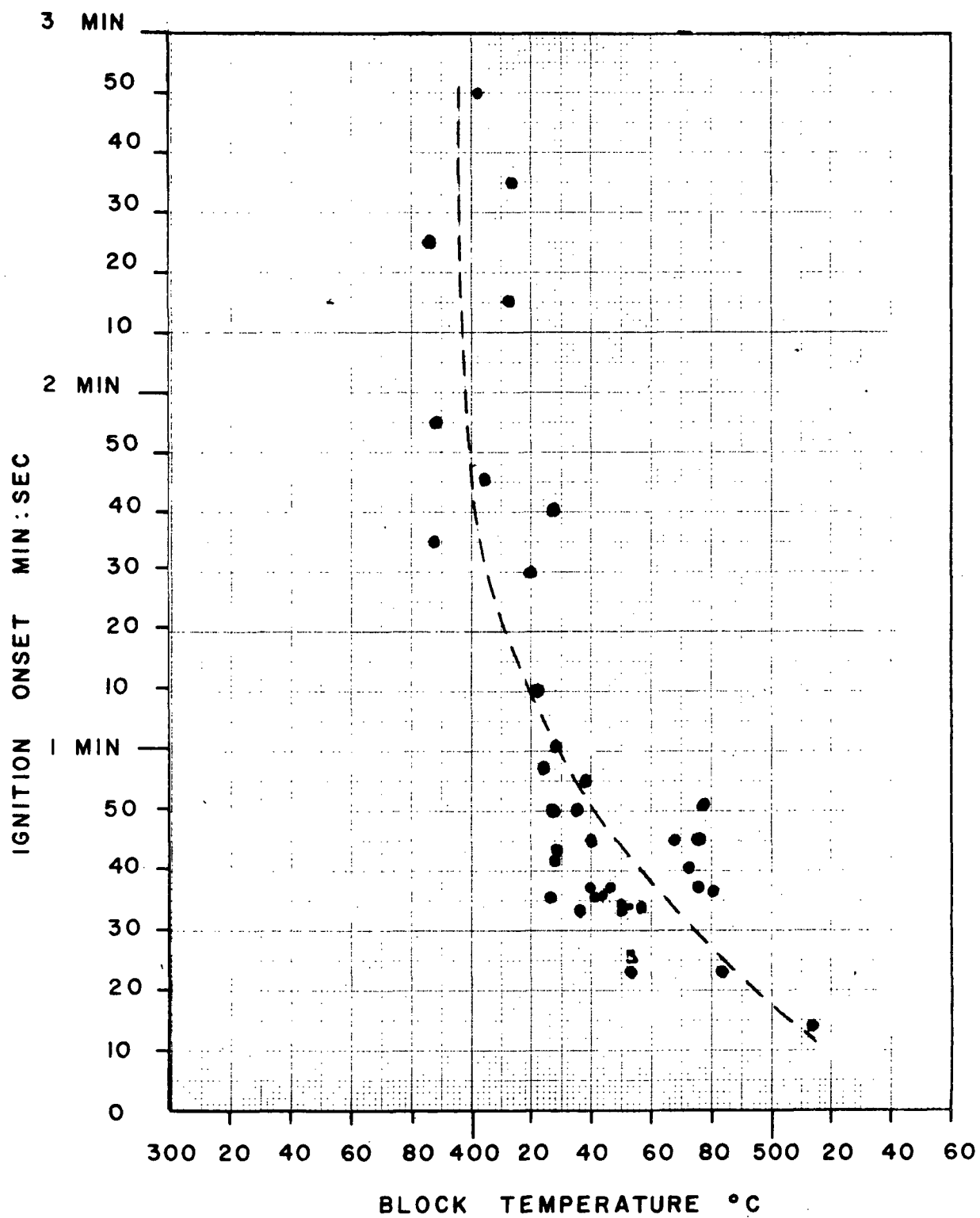


Figure 5. Ignition Delay Data Oxygen - Delrin Studies.

TABLE II. - SUMMARY OF EXPERIMENTS CONDUCTED ON  
DELIN IN AIR ATMOSPHERE<sup>a</sup>

Run No. (b)	Gas Temp. °C	Block Temp. °C	Ignition Onset Sec (c)	Burn Time Sec (d)	Remarks
209	590	540	50	-	---
210	590	525	70	-	---
213	590	375	n.i. <sup>e</sup>	-	---
214	590	375	n.i.	-	---
215	590	360	n.i.	-	---
216	475	350	n.i.	-	---
217	475	390	n.i.	-	---
218	475	470	n.i.	-	---
219	475	440	n.i.	-	---
221	460	460	n.i.	-	---
222	460	460	n.i.	-	---
223	460	475	n.i.	-	---
228	480	625	55	-	---
229	480	625	50	-	---
231	500	350	n.i.	-	---
232	525	490	n.i.	-	---
233	530	490	n.i.	-	---
234	530	500	n.i.	-	---
236	530	500	n.i.	-	---
246	660	600	60	-	---
247	650	600	55	-	---
248	600	590	55	-	---
249	580	600	60	-	---
250	560	570	60	-	---
251	550	600	50	-	---
252	550	610	65	-	---
253	535	600	60	-	---
254	535	590	65	-	---
255	535	580	75	-	---
256	520	530	75	-	---
257	625	530	75	-	---

TABLE II. - (Continued)

Run No. (b)	Gas Temp. °C	Block Temp. °C	Ignition Onset Sec(c)	Burn Time Sec(d)	Remarks
258	660	500	65	-	---
259	700	440	n.i.	-	---
260	700	340	n.i.	-	---
261	700	360	n.i.	-	---
262	700	375	n.i.	-	---
263	700	400	n.i.	-	---
264	700	450	n.i.	-	---
266	650	600	55	-	---
267	650	610	55	-	---
268	675	630	45	-	---
269	675	630	45	-	---
270	675	630	45	-	---
271	680	630	45	-	---
272	680	630	45	-	---
273	680	630	45	-	---
274	650	575	65	-	---
275	650	560	70	-	---
277	650	480	n.i.	-	---
278	680	575	45	-	---
279	600	390	n.i.	-	---
283	675	540	45	-	---
284	700	600	50	-	---
285	700	560	50	-	---
286	700	590	50	-	---
287	700	590	50	-	---
294	490	410	n.i.	-	---
295	490	460	n.i.	-	---
425	476	474	n.f.	n.a. <sup>f</sup>	White smoke at 60 sec; all over 2 min, 50 sec



TABLE II. - (Continued)

Run No. (b)	Gas Temp. °C	Block Temp. °C	Ignition Onset Sec(c)	Burn Time Sec(d)	Remarks
426	476	485	n.i.	n.a.	See Run No. 425
427	492	493	n.i.	n.a.	White smoke at 45 sec; all over 2 min, 7 sec
428	499	499	n.i.	n.a.	See Run No. 427
429	499	505	n.i.	n.a.	White smoke at 40 sec; all over 2 min, 5 sec
430	504	508	62	33	- - -
431	504	508	n.i.	n.a.	See Run No. 427
432	499	513	44	46	- - -
433	504	517	43	45	- - -
434	504	519	45	45	- - -
435	499	520	48	42	Sampling run
436	408	516	43	44	- - -
437	408	520	40	45	- - -
438	413	522	40	45	Sampling run

<sup>a</sup>All temperatures were recorded just prior to polymer insertion.

<sup>b</sup>In Runs 209-295 the burning times were not recorded and no observations were noted.

<sup>c</sup>Time measured from insertion of Delrin pellet.

<sup>d</sup>Time from ignition onset to conclusion of burning.

<sup>e</sup>No ignition.

<sup>f</sup>Not applicable.

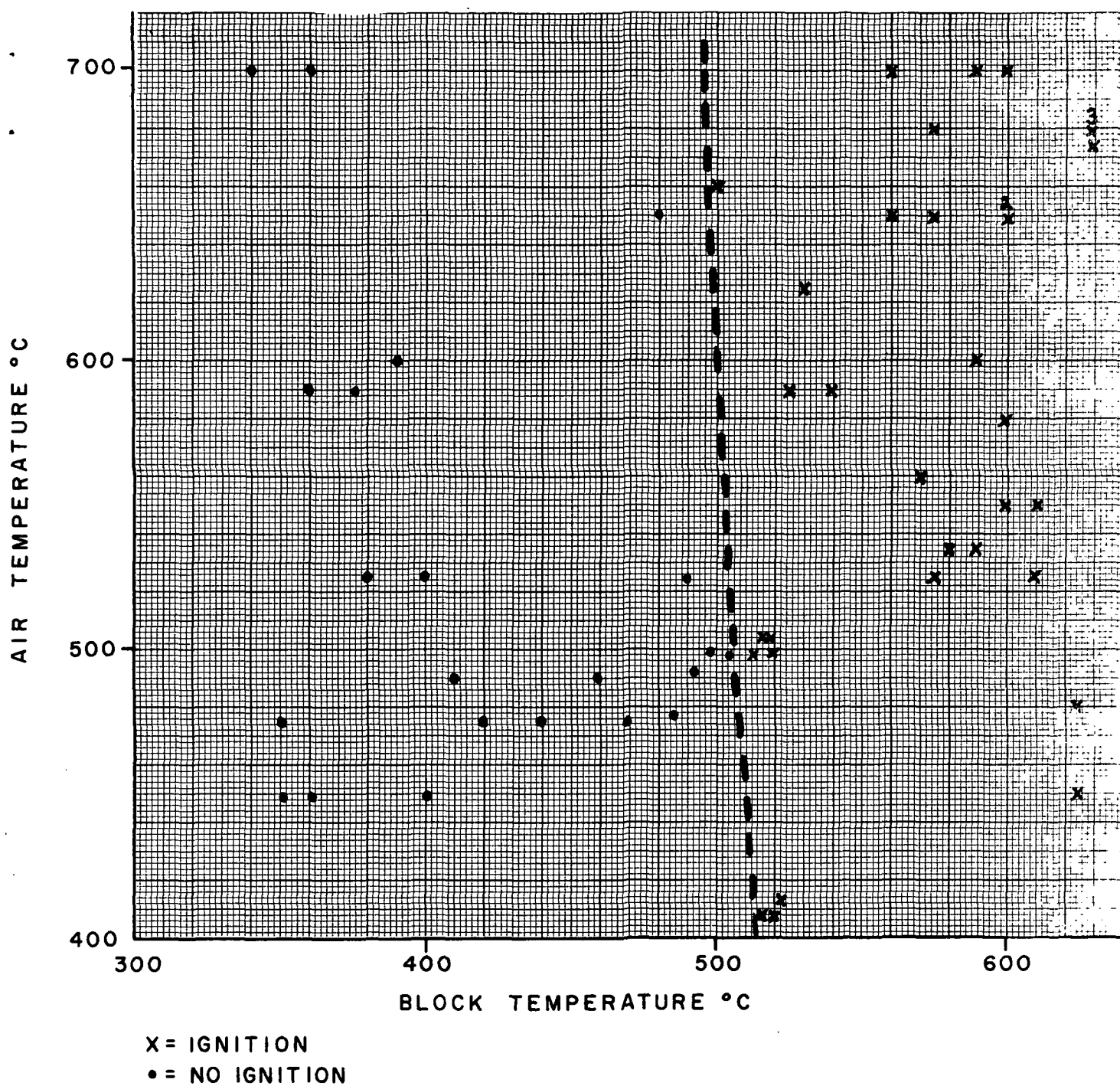


Figure 6. Effect of Polymer Heating Block and Air Temperatures Upon Delrin Ignition.

Examining Tables I and II, it can be seen that in the runs where no ignition took place, copious quantities of white smoke were evolved. This smoke had a pungent odor of formaldehyde. Formaldehyde gas is colorless and the whiteness of the smoke is actually due to the repolymerization of formaldehyde, which is in agreement with the findings of others (Refs. 1, 2, 4, 5, 6). The repolymerization should occur to a much lesser degree in argon, due to the absence of oxygen and water vapor. The tests performed in argon atmosphere (see Table III) substantiate this assumption.

To obtain a better insight into the processes taking place prior to ignition, at ignition, and during combustion, sampling was performed of the gaseous atmospheres just above the pellet. In Tables IV, V, and VI, the sampling schedules, together with the experimental details, are given for the tests conducted in oxygen, air, and argon; whereas in Tables VII, VIII, and IX, the results of the mass spectral analyses are presented.

Examining closely Tables VII and VIII (oxygen and air treatment analyses) it is clear that a certain degree of oxidation occurs prior to ignition, as can be deduced from the presence of carbon dioxide in the samples taken prior to ignition. This effect is much more pronounced in the air tests than in the oxygen experiments. The latter were performed at lower heating block temperatures although at comparable gas temperatures (e.g., compare Run 398 and Run 438). This finding would then indicate that the rate of oxidation is basically dependent on the heating block temperature, i.e., the rate of fuel production. It should be pointed out that the nitrogen percentages given for the oxygen series (Table VII) correspond to air leakage into the system; whereas in the case of the air experiments (Table VIII) the nitrogen content is the nitrogen in excess of that present in air. From this latter value the oxygen depletion can be calculated.

The striking observation in looking over the analytical data for air - Delrin tests (Table VIII) is the high percentage of hydrogen and even higher percentage of carbon monoxide. It can be deduced that these components are formed either via reaction



TABLE III.- SUMMARY OF EXPERIMENTS CONDUCTED  
ON DELRIN IN ARGON ATMOSPHERE<sup>a</sup>

Run No.	Gas Temp. °C	Block Temp. °C	Total Time Sec (b)	Remarks
417	429	437	235	Light white smoke at 60 sec
418	430	436	230	See Run No. 417
419	432	440	240	Sampling run
420	436	441	240	Sampling run
421	441	463	190	Light white smoke at 50 sec
422	427	459	192	Sampling run
423	455	465	185	Light white smoke at 48 sec
424	448	461	190	Sampling run
511	558	540	95	White smoke at 20 sec

<sup>a</sup>All temperatures were recorded just prior to Delrin insertion.

<sup>b</sup>Time required for complete evaporation of Delrin pellet.

TABLE IV.- SAMPLING SCHEDULE AND EXPERIMENTAL  
DETAILS IN THE DELRIN-OXYGEN RUNS<sup>a</sup>

Run No.	Sample No.	Sampling Time Sec (b, c)	Ignition Delay Sec (b)	Total Time Sec (d)	Gas Temp. °C	Block Temp. °C
378	1	15-20	50	87	496	428
378	2	25-30	50	87	496	428
378	3	35-40	50	87	496	428
398	1	12-17	33	77	437	437
398	2	20-25	33	77	437	437
398	3	28-33	33	77	437	437
411	1	12-17	15	65	357	459
411	2	20-25	15	65	357	459
411	3	28-33	15	65	357	459
416	1	4-9	23	64	201	453
416	2	12-17	23	64	201	453
416	3	20-25	23	64	201	453

<sup>a</sup>All temperatures were recorded just prior to Delrin insertion.

<sup>b</sup>Times are measured from the insertion of the Delrin pellet.

<sup>c</sup>Time interval of 5 sec is the period during which the evacuated ampoule was opened to the burner atmosphere.

<sup>d</sup>Time from insertion of Delrin pellet until the conclusion of burning.

TABLE V.- SAMPLING SCHEDULE AND EXPERIMENTAL  
DETAILS IN DELRIN-AIR RUNS<sup>a</sup>

Run No.	Sample No.	Sampling Time Sec(b, c)	Ignition Delay Sec (b)	Total Time Sec (d)	Gas Temp. °C	Block Temp. °C
435	1	32-37	48	90	499	520
435	2	40-45	48	90	499	520
435	3	48-53	48	90	499	520
438	1	32-37	40	85	413	522
438	2	40-45	40	85	413	522
438	3	48-53	40	85	413	522

<sup>a</sup>All temperatures were recorded just prior to Delrin insertion.

<sup>b</sup>Times are measured from insertion of Delrin pellet.

<sup>c</sup>Time interval of 5 sec is the period during which the evacuated ampoule was opened to the burner atmosphere.

<sup>d</sup>Time from insertion of Delrin pellet to conclusion of burning.

TABLE VI.- SAMPLING SCHEDULE AND EXPERIMENTAL DETAILS  
IN THE DELRIN-ARGON RUNS<sup>a</sup>

Run No.	Sample No.	Sampling Time Sec(b, c)	Total Time Sec(b, d)	Gas Temp. °C	Block Temp. °C
419	1	30-35	240	432	440
419	2	38-43	240	432	440
419	3	46-51	240	432	440
420	1	45-50	240	436	441
420	2	53-58	240	436	441
420	3	61-66	240	436	441
422	1	15-20	192	427	459
422	2	23-28	192	427	459
422	3	31-36	192	427	459
424	1	60-65	190	448	461
424	2	68-73	190	448	461
424	3	76-81	190	448	461

<sup>a</sup>All temperatures were recorded just prior to Delrin insertion.

<sup>b</sup>Times are measured from the insertion of the Delrin pellet.

<sup>c</sup>Time interval of 5 sec is the period during which the evacuated ampoule was opened to the burner atmosphere.

<sup>d</sup>Time required for pellet to evaporate completely.

TABLE VII. - MASS SPECTRAL ANALYSES OF GASES COLLECTED DURING  
DELTRIN-OXYGEN TREATMENT

Run No.	Sample No.	Total %	O <sub>2</sub> %	CO <sub>2</sub> %	N <sub>2</sub> %	H <sub>2</sub> %	CO %	Ar % (a)	H <sub>2</sub> O %	CH <sub>2</sub> O %	HCOOH %	Total Pressure mm (b)
378	1	100.57	97.42	1.32	0.93	0.20	0.24	T	0.46	T <sup>c</sup>	n.d. <sup>d</sup>	615
378	2	100.23	97.03	1.36	1.18	0.21	0.36	0.01	0.08	T	n.d.	657
378	3	99.77	95.60	2.15	1.07	0.23	0.40	0.01	0.31	T	-	604
398	1	99.58	97.33	0.80	1.00	0.17	0.07	0.01	-	T	-	714
398	2	100.38	95.41	0.85	3.60	0.15	0.07	0.03	0.07	T	-	662
398	3	100.04	96.99	1.91	0.61	0.19	0.13	-	0.01	T	-	707
411	1	99.83	96.86	1.49	1.02	0.14	0.13	0.01	0.14	T	-	693
411	2	99.57	40.25	56.23	2.34	0.16	0.32	0.11	0.16	T	-	351
411	3	101.45	17.78	79.74	0.56	0.20	2.85	0.12	0.20	T	-	263
416	1	98.94	96.90	0.46	0.88	0.20	0.37	0.01	0.12	-	T	706
416	2	101.04	98.85	1.04	0.45	0.17	0.42	0.01	0.10	-	-	694
416	3	101.30	97.34	2.54	0.73	0.18	0.40	0.02	0.09	T	-	690

<sup>a</sup>The argon percent given is that in excess of the argon present in oxygen itself and in the oxygen combined in carbon dioxide, assuming the reaction  $\text{CO} + 1/2\text{O}_2 \rightarrow \text{CO}_2$ .

<sup>b</sup>This means the total pressure of gas in the sampling ampoule.

<sup>c</sup>Trace.

<sup>d</sup>Not determined.



TABLE VIII. - MASS SPECTRAL ANALYSES OF GASES COLLECTED  
DURING DELRIN-AIR TREATMENT

Run No.	Sample No.	Total % (a)	Air %	CO <sub>2</sub> %	N <sub>2</sub> %	H <sub>2</sub> %	CO %	Ar % (b)	H <sub>2</sub> O %	CH <sub>4</sub> %	HCHO % (e)	Total Pressure mm (f)	HCHO Solid % (g)
435	1 <sup>c</sup>	100.20	76.04	4.79	15.76	1.41	1.69	0.08	0.13	0.09	0.21	601	8.2
435	2 <sup>c</sup>	100.67	73.70	5.26	17.34	1.69	2.06	0.08	0.20	0.10	0.24	530	17.6
435	3 <sup>d</sup>	100.47	0.12	9.58	48.64	12.65	28.56	0.36	0.15	0.23	0.18	640	1.4
438	1 <sup>c</sup>	100.30	79.35	4.07	12.80	1.68	1.85	0.17	0.16	0.07	0.24	653	2.5
438	2 <sup>d</sup>	100.64	16.49	9.21	45.08	8.17	20.60	0.55	0.28	0.27	0.22	568	1.1
438	3 <sup>d</sup>	100.35	0.10	7.23	41.23	16.03	34.69	0.50	0.14	0.41	0.20	626	2.1

<sup>a</sup> Total percentage represents only the components of the gas phase without inclusion of the solid formaldehyde deposit.

<sup>b</sup> The argon percent given is that in excess of the argon present in air.

<sup>c</sup> Trace of formic acid.

<sup>d</sup> Trace of acetylene.

<sup>e</sup> Formaldehyde present in the gaseous phase.

<sup>f</sup> Total pressure of gas in the sampling ampoule.

<sup>g</sup> Solid formaldehyde deposited on the ampoule wall; the percentage is given with respect to the total pressure in the ampoule plus the pressure of the solid formaldehyde if it were vaporized.

TABLE IX.- MASS SPECTRAL ANALYSES OF GASES COLLECTED DURING  
DELIRIN-ARGON TREATMENT

Run No.	Sample No.	Total % (a)	Ar %	Air %	CO <sub>2</sub> %	N <sub>2</sub> %	H <sub>2</sub> %	CO %	H <sub>2</sub> O %	HCHO % (b)	Total Pressure mm(c)	Solid HCHO % (d)
419	1	99.02	91.33	5.14	0.35	1.15	0.31	0.36	0.14	0.24	664	3.9
419	2	99.84	96.03	1.93	0.26	0.83	0.19	0.26	0.08	0.26	591	8.6
419	3	97.11	92.43	1.48	0.36	0.76	0.31	0.42	0.09	1.26	403	6.2
420	1	102.16	91.72	6.66	0.65	2.28	0.26	0.34	1.10	0.15	621	5.3
420	2	100.23	90.76	5.93	0.58	1.80	0.23	0.50	0.13	0.30	615	13.6
420	3	98.86	93.16	2.99	0.32	1.43	0.18	0.19	0.10	0.49	588	12.3
422	1	100.61	96.24	1.12	0.19	0.83	0.45	0.58	0.06	1.14	680	3.2
422	2	100.31	96.85	0.38	0.15	0.60	0.42	0.43	0.03	1.45	548	7.6
422	3	100.38	96.47	0.56	0.15	0.50	0.38	0.46	0.07	1.89	660	1.0
424	1	99.02	88.52	3.09	0.31	1.08	0.51	1.05	0.13	4.33	476	17.3
424	2	100.83	88.98	7.83	0.30	1.80	0.43	0.55	0.20	0.74	452	18.0
424	3	99.35	79.12	9.75	0.46	1.66	0.40	0.99	0.21	6.76	655	17.5

<sup>a</sup>Total percentage represents only the components of the gas phase without inclusion of the solid formaldehyde deposit.

<sup>b</sup>Formaldehyde present in the gaseous phase.

<sup>c</sup>Total pressure of gas in the sampling ampoule.

<sup>d</sup>Solid formaldehyde deposited on the ampoule wall; the percentage is given with respect to the total pressure in the ampoule plus the pressure of the solid formaldehyde if it were vaporized.

or



in agreement with the published data (Ref. 6) which show clearly that this type of decomposition (reaction 3) occurs at temperatures above 300°C, whereas pyrolysis of Delrin below and at 300°C was found to result in formaldehyde only (Ref. 3). The higher percentage of carbon monoxide as compared to hydrogen, is to be expected in view of the more facile oxidation of H<sub>2</sub>. In Samples 435-3 and 438-3, the high contents of H<sub>2</sub> and CO are due to oxygen depletion to ca 0.02%. Accordingly, one has here a perfect case of fuel rich system. In the oxygen runs the high concentration of carbon dioxide (79.74%; Run 411, Sample 3) shows clearly that fuel (decomposing polyformaldehyde) and oxygen are at almost stoichiometric proportions.

It is obvious that upon ignition and combustion of Delrin, CO<sub>2</sub> and H<sub>2</sub>O are the main products. In the Tables VII and VIII the argon content present in oxygen and air was subtracted together with these components. Assuming that carbon dioxide in the samples is derived from the equation



we have corrected also for the argon in the CO<sub>2</sub>. In the runs taken during combustion in oxygen the amount of argon left over corresponds directly to that accounted for by CO<sub>2</sub> indicating clearly that the same amount of oxygen was lost. The only possible way this could have happened is by formation of water which could not be collected due to condensation in the sampling system. Thus, the argon here serves as the internal standard or tracer. However, in the air-Delrin tests, after accounting for the argon present in air and that associated with the oxygen in the CO<sub>2</sub>, the argon left over was found to be substantially higher than that which was accounted for by the oxygen in CO<sub>2</sub>. This supports further our deduction that hydrogen is formed originally in equal quantities with carbon monoxide, yet since it is oxidized more readily it is also faster depleted; accordingly more water than CO<sub>2</sub> is formed, resulting in turn in higher argon content.

General Conclusions: It is our belief that the dissociation of either Delrin or formaldehyde monomer into CO and  $H_2$  is the ignition determining mechanism. The manner in which ignition occurs, i.e., with rather explosive loud report, in an empirical way, also tends to support that ignition is triggered by hydrogen. Furthermore, the faster depletion of hydrogen as compared to carbon monoxide shows the oxidation of the former to be the rate governing step.

The data obtained in the Delrin-argon experiments, presented in Tables IX and X, substantiate the postulated mechanism. A portion of the tests listed in Table X, Runs 568-573 have been performed after the completion of all the other experiments, including the Teflon series. In the Runs 568-573 new, more powerful polymer heating block elements were employed and new sampling probe was used. The relatively high hydrogen values attained in these tests could be due to any of the three factors or their combination, namely: (a) more powerful heaters, yet temperatures recorded by the thermocouple were the same (b) the new probe, the change of positioning could have a critical effect (c) longer time intervals from insertion to actual sampling in the relatively low temperature experiments. However, it can be safely said that runs 568-573 can be directly compared and based on these it is obvious that hydrogen content increases rapidly with the increase in the temperature of the polymer heating block. Furthermore, the hydrogen production seems to be independent of the gas temperature. This observation is in agreement with our findings that Delrin ignition, both in oxygen and air, is apparently independent of the oxidizing gas temperature. One is strongly tempted to postulate the equation (3) for the  $H_2$  and CO dissociation; however, such a postulation in view of the limited data accumulated to date is merely a speculation.

TABLE X. - EFFECT OF TEMPERATURE ON H<sub>2</sub> AND CO  
EVOLUTION IN DELRIN-ARGON TESTS

Run No.	Gas Temp. °C	Block Temp. °C	Sampling Interval Sec	H <sub>2</sub> %	CO %
419 <sup>a</sup>	432	440	46-51	0.31	0.42
422 <sup>a</sup>	427	459	31-36	0.38	0.46
424 <sup>a</sup>	448	461	76-81	0.40	0.99
571	401	349	180-185	0.59	0.54
568	424	405	105-110	1.89	1.90
572	413	449	105-110	9.64	9.83
570	508	504	45-50	10.36	10.25
569	404	506	45-50	11.06	11.05
573	424	551	30-35	17.61	17.49

<sup>a</sup>These tests were performed using another probe and less powerful polymer heating block elements than was the case in experiments 568-573.

Teflon Investigations: - The Teflon studies were initiated in view of the fire resistant nature of this polymer. The specific objectives were to determine the ignition characteristics or limits of this material in media such as oxygen and air and to determine species evolved during preignition, ignition and combustion. The nature of these products is of utmost importance in outgassing toxicity considerations which must be taken into serious account in any utilization involving confined locations.

The Teflon-air investigations are incomplete, due to time limitation. Under the modification of the Contract NASW-1921, the air studies are proceeding presently and thus the data generated under that program are logical extensions of the work reported here.

Background Information: Teflon, polytetrafluoroethylene, is an exceptionally thermally stable organic material. Actually, it is the most thermally stable single chain, linear polymer (Ref. 7). The physical properties and types of polytetrafluoroethylene resins, commercially available, are given in E. I. DuPont de Nemours and Company, Inc., Bulletins (Ref. 8).

A large number of investigations were performed regarding the pyrolytic behavior of polytetrafluoroethylene. The most extensive studies were conducted by the group at National Bureau of Standards. References to specific aspects of this work, believed to have direct bearing on the present program, are included in the current report (Refs. 9-13). Based on these data the pyrolyses in vacuo yield as the main product the monomer ( $C_2F_4$ , 94-97%), the reaction being first order at 480-510°C. These findings were substantiated by others (Refs. 14-18). Under autogeneous pressure other products were also produced. Lewis and Naylor (Ref. 16) identified  $C_3F_6$  and  $C_4F_8$  in addition to  $C_2F_4$  whereas Jellinek and Kachi (Ref. 19) obtained mainly the dimer  $C_4F_8$ , together with small amounts of  $CO_2$  and  $SiF_4$ . In the decompositions the initiation of the chain breakdown appears to proceed via the random production of two types of radicals  $-CF_2^{\bullet}$  and  $-CF_2 - CF^{\bullet} - CF_2-$  (Ref. 13). This stipulation is further supported by the finding of Florin, et al (Ref. 10) that the thermal stability of polytetrafluoroethylene could not be improved by variation in polymerization techniques i.e., by the change of the end groups.

Pyrolyses of polytetrafluoroethylene in oxidizing atmospheres such as air and oxygen below 650°C produced  $\text{COF}_2$  as one of the main products (Refs. 20, 21). Also the discharge action upon Teflon in the presence of oxygen gave  $\text{COF}_2$  as one of the products (Ref. 22). It is noteworthy that in the absence of oxygen, but in the presence of helium (used as discharge sustaining medium) similar products were obtained as during pyrolysis performed, e.g., in nitrogen. The relative ease of oxidation of Teflon at and above the decomposition temperature is to be expected in view of the ready reaction of tetrafluoroethylene with oxygen at low temperatures (Refs. 23, 24). Also photolysis of tetrafluoroethylene (Ref. 25) in the presence of oxygen was found to yield  $\text{COF}_2$  in addition to other compounds.

Based on the work of Wall and Michaelson (Ref. 11), the pyrolysis of Teflon proceeds faster in oxygen containing atmospheres, than in the inert media, most likely due not only to the attack of oxygen upon the produced monomer but also caused by the oxygen interaction with the backbone free radicals. The latter results in an increase of the effective rate of decomposition propagation. This was substantiated by the ablation studies of Graves (Ref. 26) and by our own work reported in the next section. Interestingly, during actual burning of Teflon, Fenimore and Jones (Ref. 27) proposed elemental fluorine, one of the species in the flames, to be the agent at least partly responsible for the sustained breakdown of Teflon. Michaelson and Wall (Ref. 12) found a similar effect in their pyrolytic studies conducted on polytetrafluoroethylene in the presence of fluorine atom donors such as  $\text{ClF}_3$  and  $\text{IF}_5$ . These materials appeared to ~~inhibit~~ initial decomposition; however, this action was of a short duration and was followed by the attack of fluorine atoms resulting in scissions through metathetical reactions.

Experimental Results and Discussion: The Teflon investigations were performed in oxygen, air, and argon atmospheres using the stagnation burner arrangement. Two sizes of pellets were employed 1/2" x 0.05" and 1" x 0.05"; the actual weight ranges of these pellets are given in the Section "Experimental Details and Procedures." The ignition studies were conducted with the 1/2" pellet whereas for the sampling experiments, the larger size was employed.

Teflon ignition and combustion in oxygen took place in a very controlled manner, which is contrary to the action of Delrin. The Teflon-oxygen runs are summarized in Table XI and the influence of polymer heating block and oxygen temperatures upon ignition is illustrated in Figure 7. Based on these data there appears to be some dependence of ignition onset on the oxygen temperature, i.e., at oxygen temperature of 564°C ignition took place at the block temperature of 501°C whereas at oxygen temperature of 471°C the block temperature had to be increased to 525°C to effect ignition. The heating block temperature, however, seems to be the ignition determining factor. Similar effects were noted in the case of Delrin. It is noteworthy that the ignition delays for the 1/2" pellets obtained under nearly identical polymer heating block and gas temperatures were relatively constant, runs 444, 445, 447, 448, and 451 (ignition delay 70-78 sec, Table XI). The agreement was somewhat worse for the 1" pellets, runs 457-460 ignition delay 154-176 sec. The wider discrepancy in the Teflon as compared to the Delrin series is due to the use of fume hood fan in the Teflon runs (in view of the toxicity of the combustion products) resulting in temperature fluctuation. This type of an effect would be expected to be emphasized in the case of a larger sample as reflected in the comparison of the 1/2" and 1" diameter pellets.

For the sampling experiments performed in oxygen, the schedules are given in Table XII, whereas the results of mass spectral analyses are compiled in Table XIII. The samples in the run 455 were taken significantly before the actual ignition, consequently there was no CF<sub>4</sub> and only a trace of SiF<sub>4</sub>. The relatively high content of CO<sub>2</sub> (1.04%) is unexplained although others encountered it also (Ref. 13). In run 460 the first sample was taken at ignition, whereas in run 462 the last sample was taken at ignition. The main combustion products were found to be CO<sub>2</sub> and CF<sub>4</sub>. The presence of CO<sub>2</sub> and CF<sub>4</sub> is to be expected since in the absence of water at relatively modest temperatures (Ref. 28) COF<sub>2</sub> disproportionates into CO<sub>2</sub> and CF<sub>4</sub>, i.e.,



Actually this type of disproportionation is responsible for the difficulty in analyzing for fluorine in fluorocarbons (Refs. 29,30). In simplified terms



TABLE XI. - SUMMARY OF EXPERIMENTS CONDUCTED ON  
TEFLON IN OXYGEN ATMOSPHERE<sup>a</sup>

Run No.	Pellet Diam. in. (b)	Gas Temp. °C	Block Temp. °C	Ignition Onset Sec(c)	Burn Time Sec (d)	Remarks
439	1/2	403	385	n.i. <sup>e</sup>	n.a. <sup>f</sup>	Pellet removed after 14 min; no change in weight
440	1/2	450	429	n.i.	n.a.	Pellet removed after 6 min; no change in weight
441	1/2	484	473	n.i.	n.a.	Pellet removed after 8 min; lost 8 mg out of 354 mg
442	1/2	523	518	100	25	- - -
443	1/2	527	510	135	15	- - -
444	1/2	529	520	70	13	- - -
445	1/2	530	518	80	15	- - -
446	1	530	517	180	30	- - -
447	1/2	530	518	78	15	- - -
448	1/2	530	518	72	16	- - -
449	1/2	537	518	58	16	- - -
450	1/2	534	518	70	14	- - -
451	1/2	532	518	105	19	- - -
452	1/2	525	518	93	13	- - -
453	1/2	516	519	74	13	- - -
454	1/2	515	518	90	14	- - -
455	1/2	518	518	96	13	Sampling run
456	1	523	523	140	24	Smoke at 85 sec
457	1	529	523	155	30	Smoke at 130 sec
458	1	530	522	176	27	- - -
459	1	530	522	174	21	- - -
460	1	532	522	154	24	Sampling run
461	1	534	525	128	22	- - -
462	1	536	523	136	29	Sampling run
463	1	389	521	n.i.	n.a.	Complete evaporation in 96 min
464	1/2	376	521	n.i.	n.a.	Complete evaporation in 37 min
466	1/2	487	483	n.i.	n.a.	Pellet removed after 10 min

TABLE XI. - (Continued)

Run No.	Pellet Diam. In. (b)	Gas Temp. °C	Block Temp. °C	Ignition Onset Sec(c)	Burn Time Sec(d)	Remarks
467	1/2	511	481	n.i.	n.a.	Pellet removed after 10 min
468	1/2	544	485	n.i.	n.a.	Pellet removed after 10 min
469	1/2	560	491	n.i.	n.a.	Pellet allowed to evaporate
470	1/2	567	512	85	15	- - -
471	1/2	564	501	143	11	- - -
472	1/2	562	493	n.i.	n.a.	Pellet removed after 10 min; about 1/2 pellet had evaporated
473	1/2	516	500	n.i.	n.a.	Pellet allowed to evaporate
474	1/2	527	514	123	13	- - -
475	1/2	525	507	n.i.	n.a.	Pellet removed after 10 min
476	1/2	471	518	n.i.	n.a.	Pellet allowed to evaporate
477	1/2	492	531	75	12	- - -
478	1/2	501	529	85	12	- - -
479	1/2	471	525	123	13	- - -
480	1/2	443	525	n.i.	n.a.	Pellet allowed to evaporate
481	1/2	485	529	83	11	- - -
482	1/2	467	499	n.i.	n.a.	Pellet removed after 10 min
483	1/2	494	503	n.i.	n.a.	Pellet removed after 10 min
484	1/2	513	518	110	16	- - -
485	1/2	513	513	169	13	- - -
505	1	534	532	70	30	- - -
506	1	541	536	88	22	- - -
507	1	539	535	85	22	- - -

<sup>a</sup>All temperatures were recorded just prior to Teflon insertion.

<sup>b</sup>All the pellets were 0.05" thick.

<sup>c</sup>Time measured from the insertion of the Teflon pellet.

<sup>d</sup>Time from ignition onset to conclusion of burning.

<sup>e</sup>No ignition.

<sup>f</sup>Not applicable.

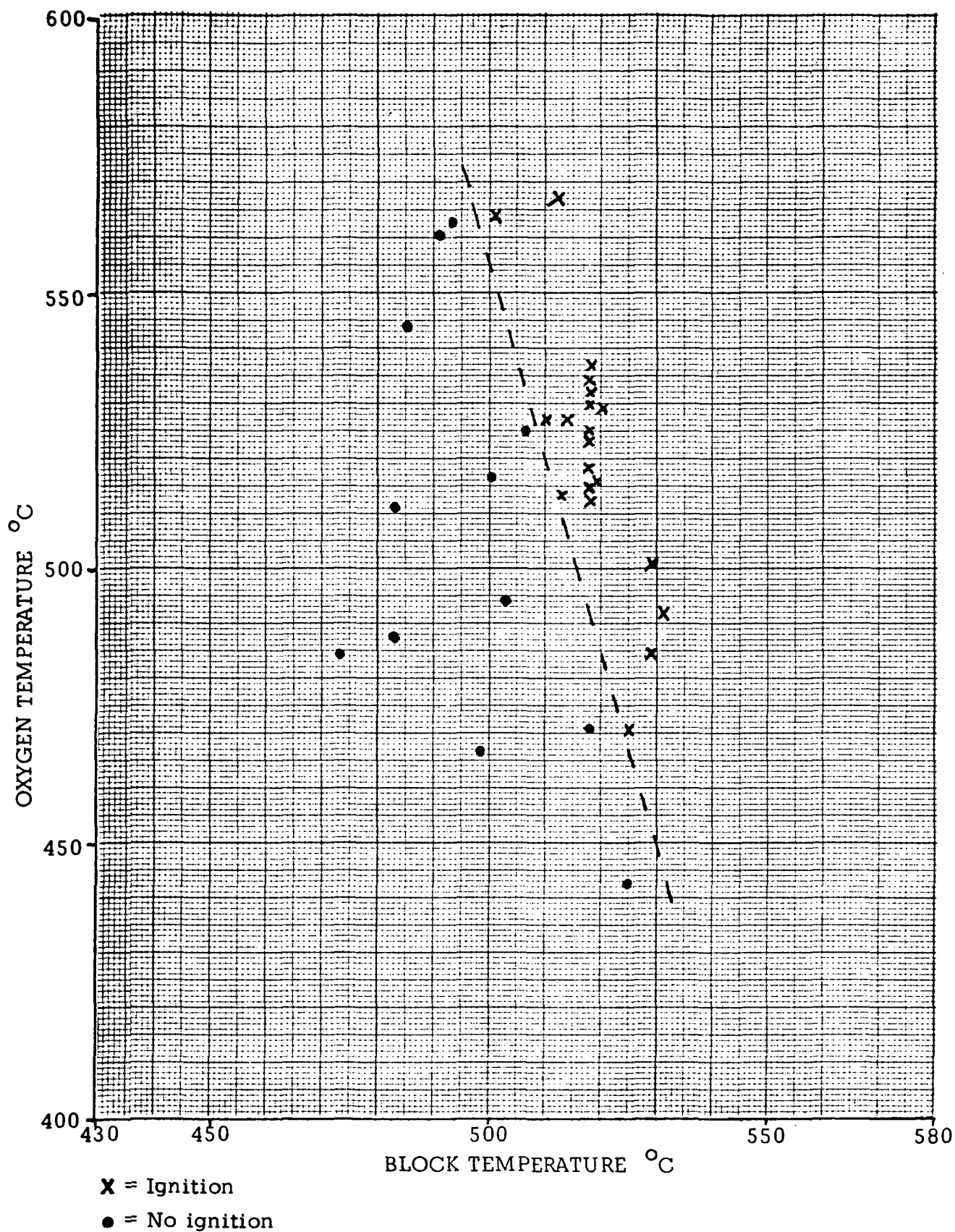


Figure 7. Effect of Polymer Heating Block and Oxygen Temperatures Upon Teflon Ignition.

TABLE XII.- SAMPLING SCHEDULE AND EXPERIMENTAL DETAILS  
IN THE TEFLON-OXYGEN RUNS<sup>a</sup>

Run No. (b)	Sample No.	Sampling Time-Sec (c,d)	Ignition Delay Sec (d)	Total Time Sec (e)	Gas Temp. °C	Block Temp. °C
455	1	49-54	96	109	518	518
455	2	57-62	96	109	518	518
455	3	65-70	96	109	518	518
460	1	155-160	154	178	532	522
460	2	163-168	154	178	532	522
460	3	171-176	154	178	532	522
462	1	119-124	136	165	536	523
462	2	127-132	136	165	536	523
462	3	135-140	136	165	536	523

<sup>a</sup>All temperatures were recorded just prior to the insertion of the Teflon pellet.

<sup>b</sup>In Run R-455 1/2" pellet was employed, whereas in R-460 and R-462, 1" pellets were used.

<sup>c</sup>Times are measured from the insertion of the Teflon pellet.

<sup>d</sup>Time interval of 5 sec is the period during which the evacuated ampoule was opened to the burner atmosphere.

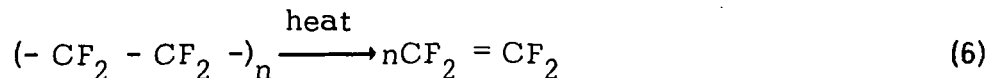
<sup>e</sup>Time from the insertion of the Teflon pellet until the conclusion of burning.

TABLE XIII. -MASS SPECTRAL ANALYSES OF GASES COLLECTED  
DURING TEFLON-OXYGEN TREATMENT

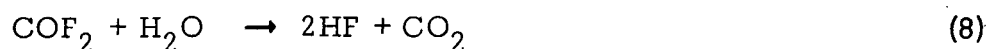
Run No.	Sample No.	Total %	O <sub>2</sub> %	CO <sub>2</sub> %	N <sub>2</sub> %	Ar %	SiF <sub>4</sub> %	CF <sub>4</sub> %	COF <sub>2</sub> %	CO %
455	1	99.24	73.74	0.15	24.83	0.21	-	-	-	0.31
455	3	100.17	87.60	1.04	11.53	-	Trace	-	-	-
460	1	100.62	47.80	19.98	12.63	0.13	1.54	15.98	2.56	n.d. <sup>a</sup>
460	2	101.04	52.55	16.03	14.85	0.14	1.82	13.01	2.64	n.d.
460	3	100.74	74.96	0.40	24.92	0.20	0.12	0.14	-	-
462	1	100.21	91.76	0.86	7.08	-	0.10	0.15	0.26	-
462	2	99.28	90.39	0.99	7.02	-	0.20	0.18	0.50	n.d.
462	3	99.09	52.07	19.86	3.86	-	1.04	18.64	3.62	n.d.

<sup>a</sup>Carbon monoxide could not be determined in the presence of carbonyl fluoride.

the overall process can be expressed as follows:



This is a simplified version since the direct oxidation of the polymer chain cannot be eliminated (Refs. 11,26). Regarding silicon tetrafluoride, this is derived from the reaction of hydrogen fluoride with silica (glass ampoules); the latter is in turn produced by hydrolysis of  $COF_2$ , i.e.,



Consequently for each  $SiF_4$  molecule formed one should obtain two molecules of  $CO_2$ . If there were no  $SiF_4$  present the amounts of  $CO_2$  and  $CF_4$  would be expected to be the same. In sample 1, run 460, 19.98 mole per cent of  $CO_2$  and 15.98 mole per cent of  $CF_4$  was obtained. Considering that 15.98 mole per cent of  $CO_2$  is derived from  $COF_2$  disproportionation one is left with  $19.98 - 15.98 = 4.0$  mole per cent of additional  $CO_2$ . The 1.54 mole per cent of  $SiF_4$  formed corresponds to 3.0 mole per cent of  $CO_2$ , which leaves the origin of the remaining 1 mole per cent of  $CO_2$  unknown. On the other hand considering the experimental errors in calculation of each of the components the agreement is not really bad. Performing the same calculation for sample 2, run 460 one is left with too little  $CO_2$  (0.6 mole per cent). It should be added that the low  $N_2$  concentration in run 462 (indicative of low air contamination) was achieved since the fume hood was switched off during this particular sampling.

We were unable to find a published breakdown pattern of  $COF_2$ ; or rather, the one which we were able to find (Ref. 31) was clearly not of pure  $COF_2$  but a mixture of  $CO_2$ ,  $SiF_4$  and some fluorocarbons. Based on the paper by Porter and Cady (Ref. 32) the 100% peak should be at  $m/e = 47$ .

From our own mass spectra of the combustion mixtures we were able to calculate the approximate breakdown pattern of  $\text{COF}_2$ , which is given in Table XIV.

It should be pointed out that none of the samples collected in the oxygen atmosphere contained any tetrafluoroethylene which is to be expected in view of its ready reaction with oxygen (Refs. 23, 24). The mass spectra were run only just beyond  $m/e = 100$  and the abundances at  $m/e = 100$  were negligible. This indicates the absence of  $\text{C}_3\text{F}_6$  and  $\text{C}_4\text{F}_8$ ; whether any  $\text{C}_2\text{F}_6$  and  $\text{C}_3\text{F}_8$  were formed is unknown since the abundances at  $m/e = 119$  were not determined.

Only a limited number of Teflon tests were conducted in air and argon. In air no ignition was observed with Teflon up to  $600^\circ\text{C}$  (both heating block and gas), however the rate of evaporation or decomposition was significantly increased at higher temperatures. These data are summarized in Table XV, whereas the sampling schedule is given in Table XVI. The evidence that Teflon decomposition into tetrafluoroethylene was accompanied by oxidation is evident from the mass spectral analyses presented in Table XVII. It is noteworthy that at corresponding temperatures the decomposition rate in air was significantly higher than in argon (compare Tables XV and XVIII), which would be expected in view of the oxidation. Even in argon, due to the open system, some oxidation took place as evidenced by the presence of small amounts of  $\text{CO}_2$  (see Table XX). The gas composition data for Teflon-air and Teflon-argon runs presented in Tables XVII and XX are not completely correct, since as in the oxygen tests the mass spectra were run only just beyond  $m/e = 100$ . After accounting for tetrafluoroethylene in runs 493 and 496 (based on  $m/e = 81$ ) a significant number of divisions were left over at  $m/e = 100$ . This points to the presence of perfluoropropene and octafluorocyclobutane (tetrafluoroethylene dimer). Whether any of the saturated fluorocarbons such as hexafluoroethane and octafluoropropane were formed is unknown. In analogy with the studies performed by others (Refs. 14, 16) under autogenous pressures one would expect these materials to be formed. The presence of the saturated fluorocarbons, which have a considerable abundance at  $m/e = 69$  (taken in our work as the base peak for  $\text{CF}_4$ ) will decrease the reported percentage of

TABLE XIV. - BREAKDOWN PATTERN OF COF<sub>2</sub>

<u>m/e</u>	<u>Relative Intensity</u>
12	12.5
19	3.1
31	6.7
47	100
50	3.3
66	72.9



TABLE XV. -SUMMARY OF EXPERIMENTS CONDUCTED ON  
TEFLON IN AIR ATMOSPHERE<sup>a</sup>

Run No.	Pellet Diam. In. (b)	Gas Temp. °C	Block Temp. °C	Remarks
486	1/2	576	540	No ignition; complete evaporation in 15 min.
487	1/2	590	555	No ignition; complete evaporation in 7 min 30 sec.
488	1/2	600	565	No ignition; complete evaporation in 5 min 40 sec.
489	1/2	601	568	No ignition; complete evaporation in 4 min 45 sec.
490	1/2	613	577	No ignition; complete evaporation in 4 min 15 sec.
491	1/2	586	585	No ignition; complete evaporation in 4 min 25 sec.
492	1	588	586	No ignition; complete evaporation in 4 min 30 sec.
493	1	600	595	Sampling run; no ignition; complete evaporation in 4 min 10 sec.

<sup>a</sup>All temperatures were recorded just prior to the insertion of the Teflon pellet.

<sup>b</sup>All the pellets were 0.05" thick.

TABLE XVI.- SAMPLING SCHEDULE AND EXPERIMENTAL  
DETAILS IN THE TEFLON AIR RUNS<sup>a</sup>

Run No.	Sample No.	Sampling Time, Sec. (b,c)	Total Time, Sec. (b,d)	Gas Temp. °C	Block Temp. °C
493	1	120-125	250	600	595
493	2	130-135	250	600	595
493	3	140-145	250	600	595

<sup>a</sup>All temperatures were recorded just prior to the insertion of the Teflon pellet.

<sup>b</sup>Times are measured from the insertion of Teflon pellet.

<sup>c</sup>Time interval of 5 sec is the period during which the evacuated ampoule was opened to the burner atmosphere.

<sup>d</sup>Time required for complete evaporation of the Teflon pellet.

TABLE XVII.-MASS SPECTRAL ANALYSES OF GASES COLLECTED  
DURING TEFLON-AIR TREATMENT

Run No.	Sample No.	Total %	Air %	CO <sub>2</sub> %	N <sub>2</sub> %	Ar %	CF <sub>4</sub> %	C <sub>2</sub> F <sub>4</sub> %	SiF <sub>4</sub> %	COF <sub>2</sub> % (a)
493	1	100.21	85.70	2.84	7.51	0.10	1.42	1.08	0.81	0.75
493	2	100.44	81.32	3.87	9.68	0.13	1.94	1.31	1.25	0.94
493	3	100.32	80.50	3.10	10.69	0.11	1.96	1.50	0.94	1.52

<sup>a</sup>Carbon monoxide could not be determined in the presence of carbonyl fluoride.

TABLE XVIII. - SUMMARY OF EXPERIMENTS CONDUCTED ON  
TEFLON IN ARGON ATMOSPHERE<sup>a</sup>

Run No.	Pellet Diam. In (b)	Gas Temp. °C	Block Temp. °C	Remarks
465	1	527	514	Sampling Run; complete evaporation in 155 min.
494	1/2	634	599	Complete evaporation in 6 min 20 sec.
495	1	635	599	Complete evaporation in 6 min 30 sec.
496	1	639	600	Sampling run; complete evaporation in 6 min.

<sup>a</sup>All temperatures were recorded just prior to the insertion of the Teflon pellet.

<sup>b</sup>All the pellets were 0.05" thick.

TABLE XIX.- SAMPLING SCHEDULE AND EXPERIMENTAL  
DETAILS IN THE TEFLON ARGON RUNS<sup>a</sup>

Run No.	Sample No.	Sampling Time (Min;Sec) (b, c)	Total Time Min (d)	Gas Temp. °C	Block Temp. °C
465	1	23:45-23:50	155	527	514
465	3	24:05-24:10	155	527	514
496	1	3:00-3:05	6	639	600
496	2	3:10-3:15	6	639	600
496	3	3:20-3:25	6	639	600

<sup>a</sup>All temperatures were recorded just prior to the insertion of the Teflon pellet.

<sup>b</sup>Times are measured from the insertion of Teflon pellet.

<sup>c</sup>Time interval of 5 sec is the period during which the evacuated ampoule was opened to the burner atmosphere.

<sup>d</sup>Time required for pellet to evaporate completely.

TABLE XX.- MASS SPECTRAL ANALYSES OF GASES COLLECTED  
DURING TEFLON-ARGON TREATMENT

Run No.	Sample No.	Total %	Ar %	CO <sub>2</sub> %	N <sub>2</sub> %	Air %	CF <sub>4</sub> %	C <sub>2</sub> F <sub>4</sub> %	SiF <sub>4</sub> %	COF <sub>2</sub> % (a)
465	1	99.80	90.57	0.15	1.49	7.59	-	-	-	-
465	3	100.84	90.27	0.11	0.92	9.54	-	-	-	-
496	1	100.39	88.05	0.16	1.12	8.25	0.60	2.16	0.03	0.02
496	2	100.60	94.12	0.12	0.28	2.70	0.68	2.63	0.04	0.02
496	3	99.31	73.83	0.22	0.78	21.28	0.69	2.46	0.05	-

<sup>a</sup>Carbon monoxide cannot be determined in the presence of carbonyl fluoride.

carbon tetrafluoride. To obtain a better insight into the processes occurring, the air and argon experiments will be repeated under the extension of Contract NASW-1921 to determine exactly the composition of the gaseous mixture. Also under the follow-on program the ignition curve for the air-Teflon system will be obtained.

Toxic Off-Gassing Considerations and Conclusions: Based on the data presented in Tables XV and XVIII, the rough pyrolyses rates for certain tests can be calculated, assuming that the rate stays constant throughout the pyrolysis. It is known that the rates of pyrolyses do change with the duration of an experiment due to (1) changes in polymer structures (2) the thickness of the sample. The first effect is believed to be relatively unimportant in the case of polytetrafluoroethylene both in vacuum and inert atmospheres below 550°C. Yet, the thickness of the sample has a definite bearing on the rate of pyrolysis as can be seen by comparison of run 463 and 464 (see Table XI). In these two runs the temperatures involved were almost identical and the pellets were also originally of identical thickness. However, in run 462 the 1/2" diameter pellet was employed whereas in run 463 a 1" pellet was used. Teflon undergoes a transition to a rubbery gel at 327°C, thus at 521°C (heating block temperature) the material must be readily flowing, consequently able to fill up the burner recession (diameter 1.75", see Fig. 1). Accordingly, for all practical purposes the 1/2" diameter pellet at the temperature of the experiment, must be thinner than the 1" pellet. This is reflected in the pyrolysis rate of 1.04%/min for the 1" pellet as compared to 2.70%/min for the 1/2" sample. Unfortunately we do not have directly comparable tests conducted in oxygen, air, and argon. On the other hand the two runs 493 and 496 conducted respectively in air and argon atmospheres show definitely that the oxidizing atmosphere results in a faster pyrolysis rate. Thus in argon the rate is 16.7%/min; whereas in air it increases to 24%/min. This observation is in agreement with the results of Wall and Michaelsen (Ref. 11) and Graves (Ref. 26) who found that the rate of Teflon attrition is significantly increased in oxidizing media.

Based on current studies the effect of an oxidizing gas becomes noticeable only at elevated temperatures. Direct comparisons of rates in oxygen and argon atmospheres are difficult, in view of the relatively low rates of pyrolysis at temperatures close to the ignition temperatures in oxygen. This becomes obvious in examining the compositions of samples 462-1 and 462-2 taken 12 and 4 seconds prior to ignition (see Tables XII and XIII). The concentration of  $\text{COF}_2$  in the sample 462-1 is only 0.46 mole per cent, whereas in 462-2 it is 0.90 mole per cent (this includes both free  $\text{COF}_2$  and  $\text{COF}_2$  analyzed in the form of  $\text{SiF}_4$ ; see equations (8) and (9). It is noteworthy that in sample 455-2 where sampling was performed more than 30 sec prior to ignition (see Table XI) no  $\text{COF}_2$  and  $\text{SiF}_4$  could be detected (see Table XII).

Comparing tests conducted in argon and air at corresponding temperatures, Run 496 and 493, it is quite apparent that in air at sufficiently high temperatures, yet in the absence of combustion,  $\text{COF}_2$  concentration of considerable magnitude is reached. The toxic nature of this compound has been amply documented (Refs. 21, 33). Elaborating further, the content of  $\text{COF}_2$  in the sample 493-3 was 3.4% (assuming all the  $\text{SiF}_4$  to be  $\text{COF}_2$  derived). The average value of  $\text{COF}_2$  produced during actual Teflon combustion in oxygen was ca 5.9% only roughly double the value of outgassing in air (see Table XIII, Sample 460-1 = 5.64%; 460-2 = 6.28%; 462-3 = 5.70%), although the concentration of  $\text{CO}_2$  and  $\text{CF}_4$  was almost an order of magnitude higher. In run 493 the average rate of pyrolysis was 5.6 mg/sec (Table XV), and on the basis of the analysis sample 493-3 (Table XVII) this corresponds to the production of 2.721 mg  $\text{COF}_2$ /sec or 0.15% Teflon/sec is changed into  $\text{COF}_2$  (again assuming that all the  $\text{SiF}_4$  is  $\text{COF}_2$  derived). These rather incomplete data tend to show the inherent danger of Teflon toxic outgassing which does occur unaccompanied by burning, when the material is subjected to sufficiently high temperatures. Such temperatures can be reached due to overheated electric wires and other conditions in the absence of actual flames. It is noteworthy that the level of  $\text{COF}_2$ , under these conditions, can account for almost half of the pyrolyzed material.

## Theoretical Considerations

General Conditions. - Ignition and combustion of initially unmixed reactants have been first studied based on boundary layer approximations and similar techniques (Ref. 34,35). Ignition and combustion of vaporizing liquid fuel have also been investigated based on equilibrium and frozen flow approximations and numerical techniques (Ref. 36, 37, 38). The analysis is presently being extended to study the ignition and combustion of polymers. Consider the flow configuration depicted below:

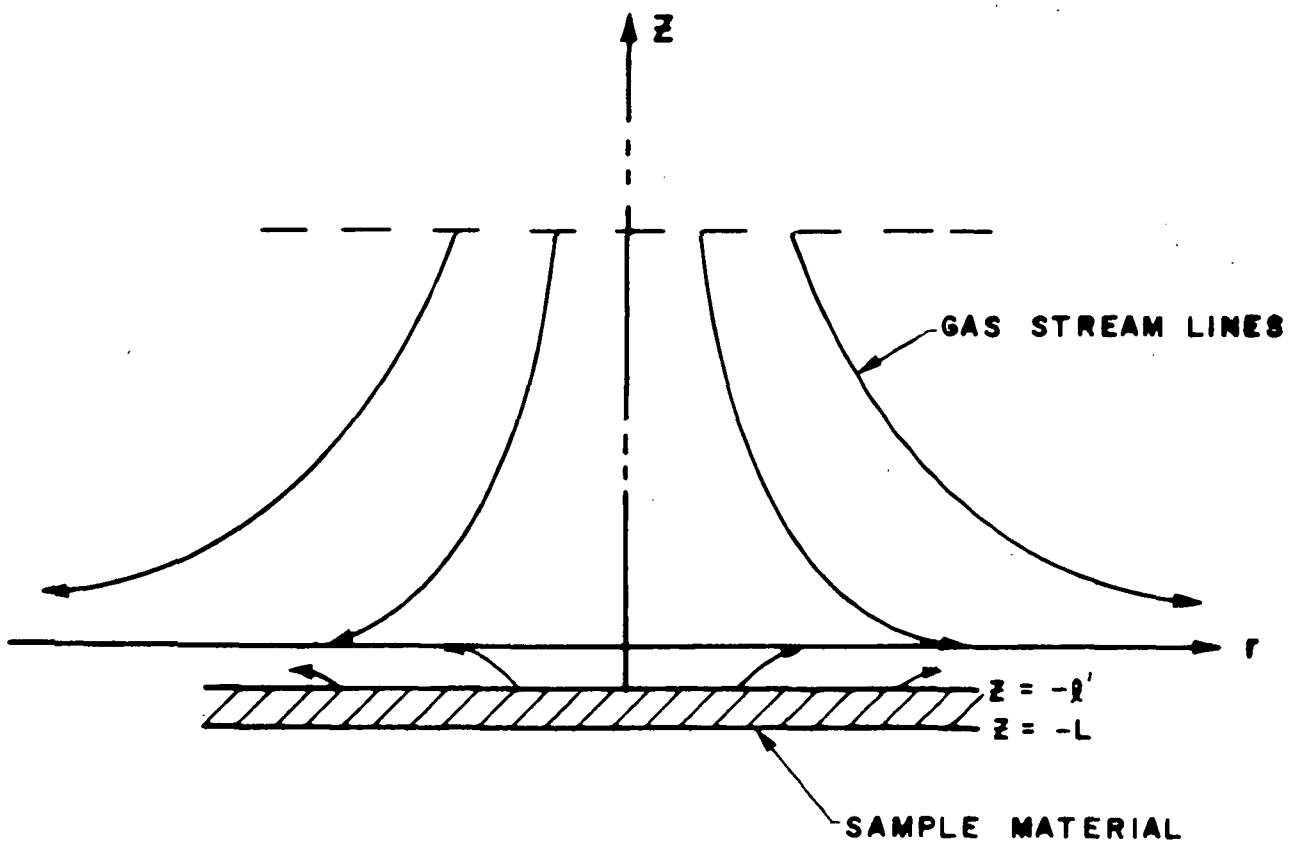


Figure 8. Flow Configuration

Here the oxidizing gas is introduced to flow over the polymer in a direction perpendicular to the material surface. Under these conditions reactions are assumed to occur between the oxidizing gas and the pyrolytic gas products. Reactions between the polymer and the oxidizing gas on the material surface are assumed to be negligible.

### Governing Equations. -

#### Continuity Equation:

Based on the flow field configuration of Figure 8, the tangential velocity  $v'$  in the  $\theta'$  direction as well as quantities varying in the  $\theta'$  direction,  $\partial/\partial\theta'$ , are both equal to zero. Denoting  $u'$  and  $w'$  as the velocities in the  $r'$  and  $z'$  directions, and  $\rho'$  as the density of the gas mixture, the continuity equation can be written as

$$\frac{\partial}{\partial r'} (\rho' u' r') + \frac{\partial}{\partial z'} (\rho' w' r') = 0 \quad (10)$$

Considering a gas mixture to consist of  $n$  different gas species,  $i=1, 2, 3, \dots, n$  and defining  $\rho'_i$  as the density of gas species  $i$ , the continuity equation for species  $i$  becomes

$$\frac{\partial}{\partial r'} (\rho'_i u'_i r') + \frac{\partial}{\partial z'} (\rho'_i w'_i r') = r' \omega'_i \quad (11)$$

where  $\omega'_i$  is the rate at which gas species  $i$  are being produced.

Defining  $\kappa'_i$ ,  $u'_i$ , and  $w'_i$  as

$$\kappa'_i = \frac{\rho'_i}{\rho'}$$

$$u'_i = u' + U'_i \quad (12)$$

$$w'_i = w' + W'_i$$

where  $U'_i$  and  $W'_i$  are the diffusion velocities of species  $i$ , equation (11) can be written as

$$\rho' u' \frac{\partial \kappa'_i}{\partial r'} + \rho' w' \frac{\partial \kappa'_i}{\partial z'} = -\frac{1}{r'} \frac{\partial}{\partial r'} (\rho' \kappa'_i r' U'_i) - \frac{\partial}{\partial z'} (\rho' \kappa'_i W'_i) + \omega'_i \quad (13)$$



$(\rho' \kappa_i r' U_i', \rho' \kappa_i r' W_i')$  are the mass diffusion components with respect to the mean gas flow. Defining  $j_{i,r'}$  and  $j_{i,z'}$  as

$$j_{i,r'} = \rho' \kappa_i U_i' \quad (14)$$

$$j_{i,z'} = \rho' \kappa_i W_i'$$

the diffusion components can be related to the density concentration  $\kappa_i$  as

$$\begin{aligned} \frac{\partial}{\partial r'} (\kappa_i) &= \frac{1}{\rho} \sum_{j=1}^n \frac{M^2}{M_j M_i} \frac{\kappa_j j_{i,r'} - \kappa_i j_{j,r'}}{D_{j,i}} \\ \frac{\partial}{\partial z'} (\kappa_i) &= \frac{1}{\rho} \sum_{j=1}^n \frac{M^2}{M_j M_i} \frac{\kappa_j j_{i,z'} - \kappa_i j_{j,z'}}{D_{j,i}} \end{aligned} \quad (15)$$

$M_i$  and  $M$  are the molecular weight of species  $i$  in the gas mixture.

Momentum Equations:

Momentum equations along the radial and axial direction are

$$\rho' u' \frac{\partial u'}{\partial r'} + \rho' w' \frac{\partial u'}{\partial z'} = - \frac{\partial P'}{\partial r'} + \frac{\partial}{\partial r'} (\tau'_{r'r'}) + \frac{\partial}{\partial z'} (\tau'_{r'z'}) + \frac{2\mu'}{r'} \left( \frac{\partial u'}{\partial r'} - \frac{u'}{r'} \right) \quad (16)$$

$$\rho' u' \frac{\partial w'}{\partial r'} + \rho' w' \frac{\partial w'}{\partial z'} = - \frac{\partial P'}{\partial z'} + \frac{1}{r'} \frac{\partial}{\partial r'} (r' \tau'_{r'z'}) + \frac{\partial}{\partial z'} (\tau'_{z'z'}) \quad (17)$$

$P'$  is the local gas pressure. The rates of stress are defined as

$$\begin{aligned} \tau'_{r'r'} &= 2\mu' \frac{\partial u'}{\partial r'} - \frac{2\mu'}{3} \left( \frac{1}{r'} \frac{\partial}{\partial r'} (r' u') + \frac{\partial w'}{\partial z'} \right) \\ \tau'_{r'z'} &= \mu' \left( \frac{\partial u'}{\partial z'} + \frac{\partial w'}{\partial r'} \right) \\ \tau'_{z'z'} &= 2\mu' \frac{\partial w'}{\partial z'} - \frac{2\mu'}{3} \left( \frac{1}{r'} \frac{\partial}{\partial r'} (r' u') + \frac{\partial w'}{\partial z'} \right) \end{aligned} \quad (18)$$

### Energy Equation:

Denoting the enthalpy of the gas species  $i$  as  $h'_i$

$$h'_i = \int \frac{T'}{T_o} C_{p_i} dT + h_i^o \quad (19)$$

where  $h_i^o$  is some reference enthalpy at temperature  $T_o$  for species  $i$ , and  $C_{p_i}$  is the specific heat, the enthalpy of the gas mixture can thus be defined as

$$h' = \sum \alpha_i h'_i \quad (20)$$

Neglecting radiation effects and assuming kinetic energy and viscous dissipation terms to be relatively small as compared with thermal energies and reference enthalpies  $h_i^o$ , the energy equation can be written as:

$$\begin{aligned} \rho' u' \frac{\partial h'}{\partial r'} + \rho' w' \frac{\partial h'}{\partial z'} = \frac{1}{r'} \frac{\partial}{\partial r'} (r' k' \frac{\partial T'}{\partial r'} - r' \sum j_{i,r} h'_i) \\ + \frac{\partial}{\partial z'} (k' \frac{\partial T'}{\partial z'} - \sum j_{i,z} h'_i) \end{aligned} \quad (21)$$

The equation of state, for a mixture of ideal gas, can be expressed as:

$$P' = \rho' \bar{R} T' \quad (22)$$

where

$$\bar{R} = \sum \frac{R}{M_i} \alpha_i$$

It is convenient to express the quantities in terms of nondimensionalized variables, defined as follows:

$$\begin{aligned} u &= u'/u_o \\ w &= w'/w_o \\ \rho &= \rho'/\rho_o \\ \rho_i &= \rho'_i/\rho_o \\ J_{i,r} &= j_{i,r}'/\rho_o u_o \\ J_{i,z} &= j_{i,z}'/\rho_o u_o \\ h &= h'/C_{p_o} T_o \\ h_i &= h'_i/C_{p_o} T_o \\ T &= T'/T_o \\ P &= P'/\rho_o u_o \\ r &= r'/r_o \end{aligned} \quad (23)$$

$$\begin{aligned}
z &= z'/r_o \\
\omega_i &= \omega_i/\rho_o (u_o/r_o) \\
D'_{i,j} &= D'_{i,j}/D_o \\
\mu &= \mu'/\mu_o \\
k &= k'/k_o
\end{aligned}$$

Thus in terms of nondimensionalized variables, the governing equation becomes

$$\frac{\partial}{\partial r}(\rho u r) + \frac{\partial}{\partial z}(\rho w r) = 0 \quad (24)$$

$$\rho u \frac{\partial \chi_i}{\partial r} + \rho w \frac{\partial \chi_i}{\partial z} = -\frac{1}{r} \frac{\partial}{\partial r} (r J_{i,r}) - \frac{\partial}{\partial z} (J_{i,z}) + \omega_i \quad (25)$$

where  $J_{i,r}$ ,  $\chi$  and  $J_{i,z}$  are defined as

$$\frac{\partial}{\partial r} (\chi_k) = \frac{1}{Re Sc} \frac{1}{\rho} \sum_{j=1}^n \frac{M}{M_j M_k} \frac{\chi_j^{J_{k,r}} - \chi_k^{J_{j,r}}}{D_{j,k}} \quad (26)$$

$$\frac{\partial}{\partial z} (\chi_k) = \frac{1}{Re Sc} \frac{1}{\rho} \sum_{j=1}^n \frac{M^2}{M_j M_k} \frac{\chi_j^{J_{k,z}} - \chi_k^{J_{j,z}}}{D_{j,k}} \quad (27)$$

$$\text{and } Re = \frac{\rho_o u_o r_o}{\mu_o}, \text{ and } Sc = \frac{\mu_o}{\rho_o D_o}$$

$$\begin{aligned}
\rho u \frac{\partial u}{\partial r} + \rho w \frac{\partial u}{\partial z} = & -\frac{\partial p}{\partial r} + \frac{1}{Re} \left\{ \left[ \frac{\partial}{\partial r} \left( 2\mu \frac{\partial u}{\partial r} - \frac{2\mu}{3} \left( \frac{1}{r} \frac{\partial ru}{\partial r} + \frac{\partial}{\partial z} \right) \right) \right] \right. \\
& \left. + \frac{\partial}{\partial z} \left[ \mu \left( \frac{\partial w}{\partial r} + \frac{\partial u}{\partial z} \right) \right] + \frac{2\mu}{r} \left( \frac{\partial u}{\partial r} - \frac{u}{r} \right) \right\} \quad (28)
\end{aligned}$$

$$\begin{aligned}
\rho u \frac{\partial w}{\partial r} + \rho v \frac{\partial w}{\partial z} = & -\frac{\partial p}{\partial z} + \frac{1}{Re} \left\{ \left[ \frac{1}{r} \frac{\partial}{\partial r} r \left( \mu \frac{\partial u}{\partial z} + \mu \frac{\partial w}{\partial r} \right) \right] \right. \\
& \left. + \frac{\partial}{\partial z} \left[ 2\mu \frac{\partial w}{\partial z} - \frac{2\mu}{3} \left( \frac{1}{r} \frac{\partial}{\partial r} (r, u) + \frac{\partial w}{\partial z} \right) \right] \right\} \quad (29)
\end{aligned}$$

$$\begin{aligned}
\rho u \frac{\partial h}{\partial r} + \rho w \frac{\partial h}{\partial z} = & \frac{1}{Re Pr} \left\{ \frac{1}{r} \frac{\partial}{\partial r} \left[ rk \frac{\partial T}{\partial r} - \sum_{i=1}^n J_{i,r} h_i \right] \right. \\
& \left. + \frac{\partial}{\partial z} \left[ k \frac{\partial T}{\partial z} - \sum_{i=1}^n J_{i,z} h_i \right] \right\} \quad (30)
\end{aligned}$$

where  $Pr = \frac{\mu_o C_p}{k_o}$

$$P = \frac{1}{\gamma M^2} \rho T \sum_{i=1}^n \frac{\kappa_i}{M_i} \quad (31)$$

Boundary Conditions: The boundary conditions for  $z = \infty$  are

$$\begin{aligned} \rho &= 1 \\ u &= 0 \\ w &= 1 \\ T &= 1 \\ \kappa_i &= \kappa_i^o \\ P &= P_o / \rho_o u_o^2 \end{aligned}$$

The material is assumed to have a constant temperature  $T_m$  throughout and the temperature at  $z = -\ell$  is assumed to be

$$T(z = -\ell) = T_m / T_o \quad (32)$$

The radial velocity component at the surface  $z = -\ell$  is:

$$u(z = -\ell) = 0 \quad (33)$$

and the axial component is defined in terms of the rate of pyrolysis. The net oxidizer flow in the axial direction is  $\rho \kappa_o (w + W_o)$  where subscript  $o$  denotes the quantities pertaining to the oxidizer species. Assuming that the reaction occurs mainly in the vapor phase, this leads to the condition:

$$\rho \kappa_o (w + W_o) = 0 \quad \text{at } z = -\ell \quad (34)$$

or

$$\rho \kappa_o w + J_{o,z} = 0 \quad \text{at } z = -\ell$$

### Similarity Transformation:

Following the similarity transformation used in the stagnation flow, the governing equations (24)–(31) can be reduced to a set of ordinary differential equations by just defining:

$$\begin{aligned}\rho u &= r F(z) \\ \rho w &= H(z) \\ \rho(r, z) &= \rho(z) \\ h(r, z) &= h(z) \\ \kappa_i(r, z) &= \kappa_i(z) \\ J_{i,z}(r, z) &= J_{i,z}(z)\end{aligned}$$

The governing equations (24)–(31) can thus be expressed as

$$\frac{dH}{dz} + 2F = 0 \quad (35)$$

$$H \frac{d\kappa_i}{dz} = - \frac{d}{dz} (J_{i,z}) + \omega_i \quad (36)$$

$$\frac{d\kappa_i}{dz} = \frac{1}{\text{ReSc}} \frac{1}{\rho} \sum_{j=1}^n \frac{M_j^2}{M_j M_i} \frac{\kappa_j J_{j,z} - \kappa_i J_{i,z}}{D_{j,i}} \quad (37)$$

$$\frac{1}{r} \frac{\partial P}{\partial r} = \frac{1}{\text{Re}} \frac{d}{dz} \left( \mu \frac{d}{dz} \left( \frac{F}{\rho} \right) \right) - H \frac{d}{dz} \left( \frac{F}{\rho} \right) - \frac{F^2}{\rho} \quad (38)$$

$$\frac{\partial P}{\partial z} = \frac{1}{\text{Re}} \left[ 2\mu \frac{d}{dz} \left( \frac{F}{\rho} \right) + \frac{4}{3} \mu \frac{d}{dz} \left( \frac{H}{\rho} \right) - \frac{4}{3} \mu \frac{F}{\rho} \right] - H \frac{d}{dz} \left( \frac{H}{\rho} \right) \quad (39)$$

$$H \frac{dh}{dz} = \frac{1}{\text{ReSc}} \frac{d}{dz} \left[ k \frac{dT}{dz} - \sum_{i=1}^n J_{i,z} h_i \right] \quad (40)$$

### Inviscid Flow Approximation:

The velocity profile is symmetric with respect to the stagnation plane. This requires that the flow for  $-\ell' < z < 0$  be the mirror image of  $z > 0$ . The solution for such a flow field is identical with the well known inviscid flow where

$$u = r \quad (41)$$

Using equation (41) the Continuity equation (27) can be integrated to give

$$\rho w = - \int_0^z 2 \rho dz \quad (42)$$

It is convenient to introduce a new dimensionless variable  $\eta$  such that

$$\eta = \int_0^z \rho dz \quad (43)$$

Using equations (42) and (43) equation (37) can be expressed in terms of  $\eta$  as

$$-2\eta \frac{d\kappa_i}{d\eta} = - \frac{d}{d\eta} (J_{i,\eta}) + \frac{\omega_i}{\rho} \quad (44)$$

and

$$\rho \frac{d\kappa_i}{d\eta} = \frac{1}{\text{ReSc}} \frac{1}{\rho} \sum_{j=1}^n \frac{M_j^2}{M_j M_i} \frac{\kappa_j J_{i,\eta} - \kappa_i J_{j,\eta}}{D_{j,i}} \quad (45)$$

The energy equation (40) can similarly be reduced to

$$-2\eta \frac{dh}{d\eta} = \frac{1}{\text{RePr}} \frac{d}{d\eta} (\rho k) \frac{dT}{d\eta} - \frac{1}{\text{ReSc}} \frac{d}{d\eta} \sum_{i=1}^n J_{i,\eta} h_i \quad (46)$$

Based on inviscid flow approximations, the set of governing equations are reduced to equation (44) and equation (46) with the diffusion mass flux  $J_{i,\eta}$  defined by equation (45). It is often convenient to express the energy equation (46) in terms of temperature  $T$  only. The enthalpy  $h$  is defined as

$$h = \sum \kappa_i \int_{T_0}^T C_{pi} dT + h_i^0 \quad (47)$$

Assuming  $C_{pi} = C_p = \text{constant}$ , the energy equation (46) can be expressed as

$$-2\eta \frac{dT}{d\eta} = \frac{1}{\text{RePr}} \frac{d}{d\eta} (\rho k) \frac{dT}{d\eta} - \frac{1}{\rho} \sum \omega_i h_i^0 \quad (48)$$

Once the rate of pyrolysis and the reaction kinetics  $\omega_i$  are determined, equation (44), (45) and (48) will be integrated numerically.  $\omega_i$  will involve a critical parameter, the first Damkohler number  $D_1$  which is the ratio of a time characterizing the flow to a time characterizing the chemical activity. Following Reference 36, the maximum gas temperature will be computed for different Damkohler number  $D_1$ . Typical results as shown in Figure 9 will then be obtained.

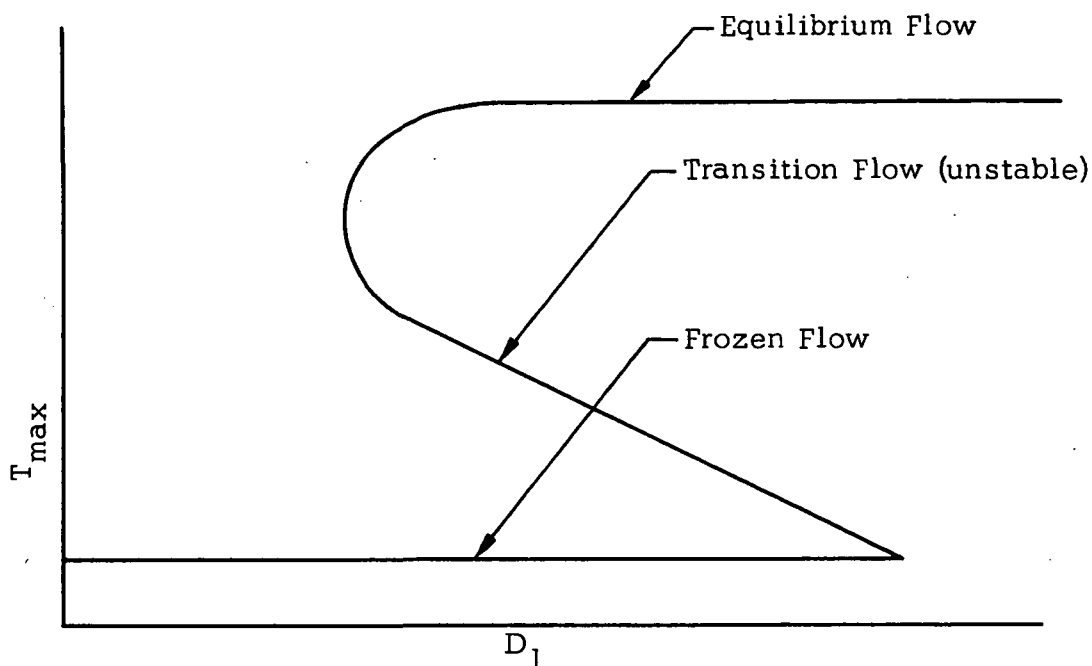


Figure 9. Variation of Maximum Temperature for Different Damkohler Numbers  $D_1$

The results will consist of a lower branch corresponding to the frozen flow and the higher branch corresponding to the equilibrium flow. The middle branch is physically unstable. A system existing under such condition will either move toward the upper or the lower branch. Ignition appears when a transition from the lower branch to the higher branch occurs. Stability analysis will determine the critical Damkohler number where such transitions will occur. Based on these results, it is possible to determine the effect of heat, mass transfer, and chemical kinetics on ignition and this can be subsequently used to correlate the experimental findings.

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